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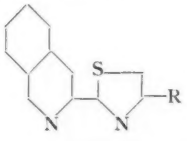
ANALOGUES OF 2,2′-BIPYRIDYL WITH ISOQUINOLINE AND THIAZOLE RINGS. PART II[1]

BY F. R. CROWNE AND J. G. BRECKENRIDGE

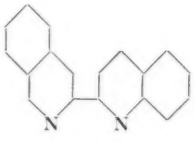
ABSTRACT

In continuation of the work reported in Part I, several more bipyridyl analogues have been prepared and the absorption spectra of the cuprous and ferrous complexes determined. The results follow the pattern of the previous series of compounds.

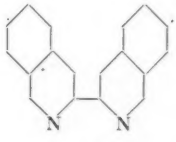
In an earlier paper (5) we reported the synthesis of a number of bipyridyl analogues and their reactions with cuprous and ferrous ion. Some of these were 1-isoquinolyl derivatives. In the present paper we report the synthesis of several analogues with the isoquinoline ring connected in the 3-position. Examples of this type in the literature are confined to 3,3′-biisoquinolyl, prepared by Case (1), who reported that it gave an orange color with ferrous ion, but gave no further details. We have repeated his synthesis, and have prepared in addition four new compounds; the structures of all these are shown below. In order to avoid confusion with those described earlier, the present compounds are numbered XVII to XXI, in continuation of the previous series.



XVII R = H
XVIII R = CH_3
XIX R = C_6H_5



XX



XXI

On the basis of our present knowledge of this type of compound, those with no "ortho" blocking groups (XVII, XXI) should react with ferrous ion, while the remainder should react only with cuprous ion; this was confirmed. Experimental work on the absorption spectra of the complexes was carried

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont.
Condensed from the M.A.Sc. thesis of F. R. Crowne.

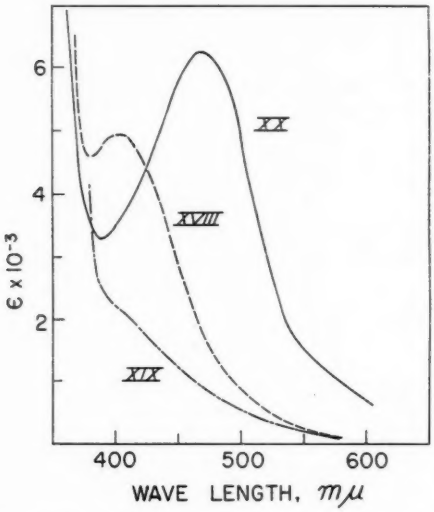
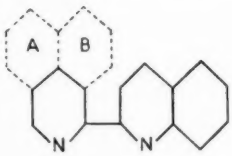


FIG. 1. Absorption spectra of copper complexes of compounds XVIII, XIX, XX.

out in the same manner as for the previous group; Fig. 1 shows the absorption spectra in the visible region for the cuprous complexes of compounds XVIII, XIX, and XX, all of which were extractable by isoamyl alcohol.

The depressing effect of a phenyl group in the "ortho" position (as compared to a methyl group) on the value for ϵ_{max} is evident (compare XVIII and XIX); this is the same as was observed in the previous series. The two compounds (XVII, XXI) with no "ortho" group gave weakly colored unstable complexes, the spectra of which were not determined. It is of interest to compare the value for ϵ_{max} for XX with that found by Hoste (3) for the isomeric 1-(2-quinolyl) isoquinoline:



Cuprous complexes
A—ϵ_{max} = 6230 at 470 mμ
B—ϵ_{max} = 2550 at 495 mμ

The fused ring in position B should not result in any appreciable hindrance to planarity, so that the steric situation in the immediate vicinity of the metal ion should be the same in both cases.

Compounds XVII and XXI behaved in a similar manner toward ferrous ion; both gave orange complexes which were highly dissociated, and we were unable to calculate accurate values for the molar extinction coefficients. The absorption spectra are shown in Fig. 2. Irving and Williams have predicted (4) that XXI should give an extractable complex with ferrous ion,

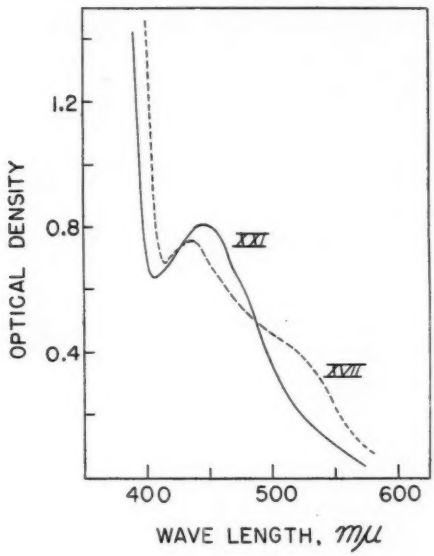


FIG. 2. Absorption spectra of iron complexes of compounds XVII, XXI.

and that it should be a more sensitive reagent than 2,2'-bipyridyl, which has a value of ϵ_{max} of 8700 at 522 mμ (6). We have confirmed this, since the complex is indeed extractable by isoamyl alcohol, and an approximate value for ϵ_{max} is 14200 at 445 mμ.

EXPERIMENTAL

Melting points are corrected: microanalyses by Micro-Tech Laboratories, Skokie, Ill.

Isoquinoline-3-aldoxime

Isoquinoline-3-carboxaldehyde, prepared from 3-methylisoquinoline by the method of Case (1), was condensed with an equimolar amount of hydroxylamine hydrochloride in aqueous ethanol. The mixture was made alkaline and poured into water, and the product recrystallized from ethanol. Yield nearly theoretical, m.p. 197–197.5°C. Calc. for $C_{10}H_8ON_2$: C, 69.75; H, 4.68; N, 16.27%. Found: C, 69.80, 69.83; H, 4.54, 4.65; N, 15.94, 16.07%.

3-Cyanoisoquinoline

The aldoxime, (19.5 gm.) was warmed with acetic anhydride (25 gm.), and after the vigorous reaction had subsided, the mixture was refluxed for two hours and then poured into water. The product was extracted with petroleum ether and recrystallized from ethanol in 80% yield, m.p. 127.5–128°C. Calc. for $C_{10}H_6N_2$: C, 77.90; H, 3.92; N, 18.17%. Found: C, 78.23, 78.34; H, 3.98, 3.97; N, 17.91, 18.00%.

Isoquinoline-3-thiocarboxamide

Five grams of the cyano compound was dissolved in 200 ml. ethanol, and ammonia was bubbled through the solution, followed by hydrogen sulphide. The yellow precipitate which appeared on standing was crystallized from ethanol. Yield theoretical, m.p. 198–198.5°C. Calc. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.80%. Found: C, 63.90, 64.14; H, 4.48, 4.40; N, 14.97, 15.13%.

3-(2-Thiazole)isoquinoline (XVII)

Isoquinoline-3-thiocarboxamide (5 gm.) and ethyl α,β-dichloroethyl ether (5 gm.) were dissolved in 230 ml. 75% ethanol and the solution refluxed for 12 hr. A further 4 gm. of the ether was added and refluxing continued for eight hours more. The solution was concentrated to 100 ml., made alkaline, and extracted with petroleum ether. Evaporation of the extract left an orange oil, which was crystallized from petroleum ether. Yield 10%, m.p. 116–117°C. Calc. for $C_{12}H_8N_2S$: C, 67.90; H, 3.80; N, 13.20%. Found: C, 67.86, 68.06; H, 3.85, 3.94; N, 12.87, 12.77%.

3-(4-Methyl-2-thiazole)isoquinoline (XVIII)
3-(4-Phenyl-2-thiazole)isoquinoline (XIX)

These were prepared by condensation of the thiocarboxamide with chloroacetone and ω-chloroacetophenone in ethanol. The products were recrystallized from ethanol; yield about 80% in both cases. Data for XVIII: m.p. 150–151°C.; calc. for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.46; N, 12.38%; found: C, 69.00, 69.01; H, 4.55, 4.53; N, 12.34, 12.11%. Picrate m.p. 184.5–185°C.; calc.; N, 15.38%; found: N, 14.92, 15.06%. Data for XIX: m.p. 173.5–174°C.; calc. for $C_{18}H_{12}N_2S$: C, 74.97; H, 4.20; N, 9.72%; found: C, 75.13, 75.15; H, 4.11, 4.16; N, 9.70, 9.84%. Picrate m.p. 191.5–192°C.; calc.: N, 13.54%; found: N, 13.40, 13.60%.

3-Acetylisoquinoline

To a Grignard reagent in ether prepared from 2.6 gm. magnesium and 14.8 gm. methyl iodide was added 11 gm. 3-cyanoisoquinoline in 600 ml. ether. The mixture was warmed gently and shaken, a voluminous precipitate appearing. Most of the ether was distilled off, 200 ml. dry benzene added, and the mixture refluxed for one hour and then cooled. Crushed ice and 50 ml. cold 50% sulphuric acid were added slowly, an orange precipitate appearing in the aqueous layer. The benzene layer was extracted with acid, and the combined acid portions made alkaline and steam-distilled. The product was recrystallized from ethanol, yield 60%, m.p. 92–92.8°C. Calc. for $C_{11}H_9ON$: C, 77.17; H, 5.30; N, 8.23%. Found: C, 77.21, 77.31; H, 5.18, 5.34; N, 8.21, 8.40%. Clemo and Popli (2) report m.p. 88°C. for this compound.

3-(2-Quinolyl)isoquinoline (XX)

To a solution of 3.4 gm. *o*-aminobenzaldehyde in 25 ml. 95% ethanol was added a solution of 4.5 gm. 3-acetylisoquinoline in 75 ml. 95% ethanol. Potassium hydroxide in ethanol (1.5 ml., 1 *N*) was added, and the mixture refluxed for two hours and cooled. The product was recrystallized from ethanol,

yield 50%, m.p. 151.5–152°C. Calc. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93%. Found: C, 84.40, 84.52; H, 4.80, 4.77; N, 11.11, 11.10%. Picrate m.p. 245.5–246°C.; calc.: N, 14.43%; found: N, 14.68, 14.55%.

ACKNOWLEDGMENT

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THE BIOGENESIS OF ALKALOIDS

X. THE ORIGIN OF THE N-METHYL GROUPS OF THE ALKALOIDS OF BARLEY[1]

By Edward Leete[2] and Léo Marion

ABSTRACT

Sodium formate-C^{14} and C^{14}-methyl-D- and L-methionine were each fed to sprouting barley under identical conditions and radioactive alkaloids were isolated from the leaves and roots. Degradation of these alkaloids showed that the D- and L-methionines were an equally efficient source of the methyl groups of N-methyltyramine and hordenine, the root alkaloids; but D-methionine was a less efficient source than L-methionine of the methyl groups of gramine, from the leaves. The formate was a source of the methyl groups of all the alkaloids, however, less efficient than the methionines, and a very poor source for the methyl groups of gramine. The significance of these results is discussed.

In view of the recent work on the biological methylation of the alkaloids hordenine (9, 14), nicotine (3, 4), ricinine (7), and protopine (18), it was of interest to see whether the N-methyl groups of the alkaloid gramine which occurs in the leaves of sprouting barley also arose from formate and methionine. The efficiency of D- and L-methionine as methyl donors was also compared. Comparatively little work has been carried out on the utilization of D-amino acids by the higher plants. In one case (19) it has been shown that while the L forms of certain amino acids produce toxic effects on *Nicotiana* species, the D-amino acids have no ill effect. With microorganisms more work has been done, some are apparently able to utilize both forms of the amino acids equally while others fail to utilize the D form, presumably owing to the absence of a D-amino acid oxidase in such organisms (11). Thus it was found (17) that *Lactobacillus arabinosus* did not utilize D-methionine whilst the same organism in the presence of pyridoxal was able to use it (5) presumably by racemization to DL-methionine via a chelate ring formation involving the pyridoxal (16).

In the present work the sodium formate-C^{14} and the C^{14}-methyl labelled D- and L-methionines were fed to identical dishes containing the germinating barley and after a suitable period the alkaloids were isolated and separated as previously described (1, 10, 12). In all cases the alkaloids were radioactive and they were degraded by established methods (12, 13) in order to locate the positions of activity. The hordenine from the formate and L-methionine feeding experiments was not degraded since previous work (14) had shown all the activity to reside in the methyl groups.

Table II shows that all the activity of the radioactive alkaloids was present in the N-methyl groups. Considering first the root alkaloids, formate is seen to be a less efficient source of methyl groups than methionine. This is in accordance with results previously obtained (3, 14) and favors the hypothesis that

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[2]*National Research Council of Canada Postdoctoral Fellow.*

formate is a precursor of the methyl groups of methionine. The D- and L-methionines are equally effective as a source of the methyl groups. The appreciably higher activity of the N-methyltyramine, which only contains one methyl group, over hordenine, which contains two, confirms the stepwise methylation (i.e., tyramine → N-methyltyramine → hordenine) since, if the N-methyltyramine were produced by the demethylation of hordenine, analogous to the formation of nornicotine from nicotine (6) in *Nicotiana glutinosa*, one would expect it to have a lower specific activity than hordenine.

In so far as gramine was concerned, D-methionine was significantly less efficient than L-methionine, and it is suggested that the leaves which are assumed to be the site of synthesis (2) are not capable of inverting the D-methionine. Thus the active gramine from the D-methionine feeding experiments results from D-methionine which has been inverted to L-methionine in the roots. The higher activity of the leaf extract (Table I) in this experiment is presumably due to D-methionine which has bypassed the enzymes causing inversion and which cannot be utilized in the leaves as a source of methyl groups. On the other hand, formate was a very poor source of methyl groups for this alkaloid. The inability of formate to serve as a precursor of N-methyl groups in ricinine has been reported by Dubeck and Kirkwood (7) who suggested that this inability was due to the state of development of the *Ricinus* plants used in their experiments. In barley, however, formate does serve as a precursor of the N-methyl groups of hordenine and N-methyltyramine, although with gramine this action is very much less marked. This might indicate that the transfer of methyl groups by formate to methionine takes place in the root but not in the leaves in which the methylation of the nitrogen of gramine can only take place by the action of methionine translocated from the roots. Such an interpretation of the result would also indicate that the enzyme systems are less developed in the leaves of barley than in the roots.

The activity of the gramine from the formate feeding experiments is of the same order as that of the gramine obtained from the feeding experiment with doubly labelled tryptophan-2-β-C^{14} in the presence of large amounts of mold (13). In the latter experiment the gramine isolated from the plant had appreciable activity in its N-methyl groups, and the postulate made then that the activity in the methyl groups had arisen by attack of the tryptophan by mold to yield formylkynurenine, which gave rise to the active formate by hydrolysis, is thus consistent with the present result.

EXPERIMENTAL

D- *and* L-C^{14}-*methyl Labelled Methionines*

S-Benzyl-DL-homocystine was resolved via the formyl derivative with brucine as described by Du Vigneaud and Patterson (8) and the two isomers converted to the methionines by treatment with sodium followed by C^{14}-methyl iodide in liquid ammonia (15).

Feeding of Labelled Substances and Isolation of the Alkaloids

L-Methionine was fed to 720 gm. of barley in 12 trays on the fourth day of germination when the shoots were 1–1.5 cm. long, the temperature of the

germination cabinets varied between 15 and 21°C. D-Methionine and formate were also fed to identical batches of barley under the same conditions. In each case the plants were harvested on the 10th day of germination, the roots and leaves separated, dried, and the alkaloids extracted as previously described (1, 10, 12). Details of the amounts of tracers fed and the yields of the various

TABLE I

WEIGHTS AND ACTIVITIES OF LABELLED SUBSTANCES FED AND ALKALOIDS ISOLATED FROM THE BARLEY (720 GM. IN EACH EXPERIMENT)*

	Tracer		
	Sodium formate	L-Methionine	D-Methionine
	Weight fed		
	22.8 mgm.	50 mgm.	50 mgm.
	Total activity		
	4.13×10^7	4.58×10^7	4.55×10^7
Roots			
Wt. of roots	113 gm.	126 gm.	113 gm.
Activity of methanol extract	8.1×10^5	5.0×10^6	7.8×10^6
Wt. of hordenine	66.5 mgm.	41.3 mgm.	77.9 mgm.
Wt. of N-methyl-tyramine	48.6 mgm.	16.4 mgm.	20.1 mgm.
Leaves			
Wt. of leaves	57 gm.	44 gm.	45 gm.
Activity of methanol extract	7.3×10^4	1.33×10^6	3.04×10^6
Wt. of gramine	65.2 mgm.	46.0 mgm.	46.2 mgm.

**Activities expressed as disintegrations per minute.*

TABLE II

ACTIVITIES OF THE ALKALOIDS AND THEIR DEGRADATION PRODUCTS*

	Tracer		
	Sodium formate	L-Methionine	D-Methionine
Hordenine	2.98×10^4	8.06×10^4	7.80×10^4
Hordenine hydrochloride	3.10×10^4	7.91×10^4	7.75×10^4
Hordenine methiodide			7.95×10^4
Methylhordenine methiodide	Not degraded	Not degraded	7.65×10^4
Trimethylamine picrate			8.10×10^4
p-Vinylanisole			0
N-Methyltyramine	9.45×10^4	1.20×10^5	1.12×10^5
N-Methyltyramine hydrochloride	10.1×10^4	1.22×10^5	1.27×10^5
Hordenine methiodide	9.45×10^4	1.21×10^5	1.11×10^5
Methylhordenine methiodide	10.0×10^4	1.23×10^5	1.04×10^5
Trimethylamine picrate	9.54×10^4	1.23×10^5	1.11×10^5
p-Vinylanisole	0	0	0
Gramine	4.38×10^3	1.72×10^5	8.61×10^4
Dimethylethylamine picrate	4.10×10^3	1.62×10^5	8.22×10^4
3-Ethoxymethylindole	0	0	0

**All activities are for carrier free material and are expressed as distintegrations per minute per millimole.*

extracts are given in Table I. Table II summarizes the results obtained on assay of the alkaloids and their degradation products obtained as previously described (12, 13).

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KINETICS OF THE REACTION $H + CH_4 = CH_3 + H_2$[1]

By M. R. Berlie[2] and D. J. Le Roy

ABSTRACT

The reaction $H + CH_4 = CH_3 + H_2$ has been studied in the temperature range 99° to 163°C. The rate constant is given by the expression $k = 1.7 \times 10^{-14} \exp(-4500/RT)$. The data are in agreement with the results, but not the interpretations, of previous work. The entropy of the methyl radical has been calculated for several temperatures.

INTRODUCTION

In a recent publication (13) preliminary data were reported for the kinetics of the reaction $H + CH_4 = CH_3 + H_2$. The significant feature of the results was the fact that the steric factor and activation energy were found to be very much lower than had been previously suspected. The results have been subjected to a careful analysis and will be presented here together with a comparison with the data obtained by other workers.

EXPERIMENTAL

The method has already been described (2, 8). Particular care was taken to purify the methane and hydrogen. Matheson C.P. methane (99.0%) was passed through two towers containing Fieser's solution, three containing concentrated sulphuric acid, and one containing Drierite. It was then subjected to trap-to-trap distillation using "pumped down" liquid air traps. The resulting gas was found to contain 0.3% ethane and 0.03% ethylene. To reduce these impurities below the limit of detection the gas was allowed to bubble slowly through liquid methane at the temperature of liquid air and then through mercury, which fixed the pressure over the liquid at approximately 20 mm. The gas was then frozen in a "pumped down" liquid air trap at −206°C. It was estimated that the final gas contained less than 0.01% impurities.

Some ethane was formed in the reaction. It was partially removed from the gas stream by passage through a "pumped down" liquid air trap; additional amounts were removed by isolating samples of the gas which came through this trap, removing the hydrogen by diffusion through a palladium thimble, and circulating the residual gas, which was largely methane, through a smaller "pumped down" liquid air trap. The total amount of ethane collected was negligible, however, in comparison with the amount of atomic hydrogen that reacted with the methane. It seems justifiable, therefore, to neglect combination of methyl radicals under the conditions used in the present experiments.

RESULTS

A number of experiments were done in the temperature range 99° to 163°C. using various pressures of methane and of molecular hydrogen. The reaction

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was considerably slower than that with ethane (2) and consequently great care had to be taken in making the correction for H atoms consumed by combination to form H_2. It has been pointed out (8) that the combination of atomic hydrogen under our experimental conditions appears to have an order between one and two. The partial pressure of methane would be expected to have an effect on the second order combination reaction, and hence the results reported here are only for experiments in which the ratio of methane to hydrogen was kept approximately constant.

The interpretation of the results is based on consideration of the following reactions:

$$H + CH_4 = CH_3 + H_2, \quad [1]$$
$$H + CH_3 (+ M) = CH_4 (+ M), \quad [2]$$
$$2CH_3 = C_2H_6, \quad [3]$$
$$CH_3 + H_2 = CH_4 + H. \quad [4]$$

In view of the negligible amount of ethane formed, reaction [3] may be neglected. If [1] were followed by [4] no H atoms would be consumed (other than by combination to form H_2). If only [1] and [2] occur then, aside from the combination reaction, the rate of consumption of H atoms would be given by the relation

$$-d(H)/dt = 2k_1(H)(CH_4). \quad (i)$$

If, in addition, [3] and/or [4] take place the value of k_1 calculated on the basis of (i) would be too small. Since it will be assumed that only [1] and [2] occur, the values of k_1 will be minimum values. If [4] occurs at all under the present experimental conditions it will become more important at the higher temperatures. This possibility will be examined more fully in the following section.

When allowance is made for first and second order combination of H atoms the rate equations take the form

$$-d(H)/dt = k_c'(H) + 2k_1(H)(CH_4), \quad (ii)$$
$$-d(H)/dt = k_c''(H)^2 + 2k_1(H)(CH_4), \quad (iii)$$

in which k_c' and k_c'' are the first and second order rate constants for H atom combination, respectively. It might be expected that k_c'' would be different for a hydrogen–methane mixture than for hydrogen alone.

As described previously (2) the H atom concentration at any position in the reactor was determined by measuring the rate of liberation of the heat of combination on the detector; this was measured as a wattage and given the symbol W. The method of determining the constant of proportionality f in the expression $(H) = fW$ has also been described (2). The reaction time t was calculated from the linear flow rate in the reactor and the distance of the detector from the point where the methane was added.

In terms of the measured quantities, equations (ii) and (iii) become

$$-dW/dt = k_c'W + 2k_1W(CH_4), \quad (iv)$$
$$-dW/dt = k_c''fW^2 + 2k_1W(CH_4). \quad (v)$$

In the integrated form they are

$$\log W = -0.4343\{k_c' + 2k_1(CH_4)\}t + \text{constant}, \quad \text{(vi)}$$

$$\log\{1 + 2k_1(CH_4)/(k_c''fW)\} = 0.4343 \times 2k_1(CH_4)t + \text{constant}. \quad \text{(vii)}$$

On the basis of (vi) log W should be a linear function of t, or for a given linear flow rate, of the distance d from the point of mixing. From (vii) a plot of log W vs. t would not be linear. A typical plot is shown in Fig. 1.

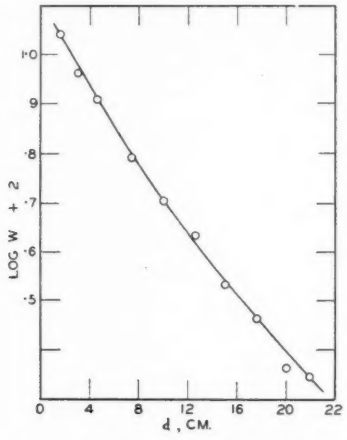

FIG. 1. Plot of log W vs. d for experiment 7Me. The linear flow rate was 98.4 cm. sec.$^{-1}$, and hence $t = d/98.4$ sec.

In Table I the values of k_1 calculated from (vi) are given the symbol k_1', those from (vii) the symbol k_1''. The means of the values calculated by the two methods are given in the last column.

TABLE I

Expt.	Temp., °C.	(H_2) $\times 10^{-15}$	(CH_4) $\times 10^{-15}$	$(H)_0$ $\times 10^{-15}$	k_c' sec.$^{-1}$	k_c'' $\times 10^{15}$ (*a*)	k_c'' $\times 10^{15}$ (*b*)	k_1' $\times 10^{17}$	k_1'' $\times 10^{17}$	k_1 $\times 10^{17}$, mean
7Ma	99	143	34.6	1.07	3.13	2.88	4.85	3.27	4.70	3.98
7Me	139	132	32.0	0.99	3.25	3.18	7.22	6.95	7.55	7.25
7Md	163	122	30.6	0.91	2.83	3.00	6.55	9.08	10.15	9.62

(*a*) *In the absence of methane.*
(*b*) *With methane present.*
Concentrations are expressed in atoms or molecules cm.$^{-3}$, k_c'' *and* k_1 *in cm.*^{3} *molecule*$^{-1}$ *sec*$^{-1}$.

The values of k_1' were obtained by subtracting the slopes of the best straight lines through log W vs. t plots for experiments with and without methane, but otherwise under identical conditions.

A lower limit for the value of k_c'' was obtained by plotting $1/W$ vs. t for an experiment with no methane present; the slope of this curve, $k_c''f$, would give

a smaller value of k_c'' than would apply to an experiment in which methane was present since, presumably, methane would be more efficient than hydrogen as a third body. A first approximation to k_1'' was the value k_1', obtained as described above. By a method of successive approximations the ratio of k_1 to k_c'' in the log term was adjusted until the best straight line fitting equation (vii) was obtained; the values of k_1'' in Table I were obtained from the slopes of such lines.

The values of the first order rate constant for the recombination of H atoms are given in column six of Table I; they are very similar to those obtained previously (8), and correspond closely with the recombination coefficient of 2×10^{-5} found by Smith (16) for a metaphosphoric acid surface. On the other hand, the second order rate constants for H atom recombination given in column seven are in fairly good agreement with the data of Farkas and Sachsse (10) quoted by Morikawa, Benedict, and Taylor (14). Their third order rate constant, 3.4×10^{16} cm.^{6} mole^{-2} sec.$^{-1}$, corresponds to a value of k_c'' of 13.4×10^{-15} cm.^{3} molecule^{-1} sec.$^{-1}$ at a hydrogen concentration of 143×10^{15} molecules cm.$^{-3}$, compared to the value 2.88×10^{-15} given in Table I.

An Arrhenius plot of the data in the last three columns of Table I is shown in Fig. 2. The following expressions are obtained from the straight line corresponding to the mean values of k_1:

$$k_1 = 1.7 \times 10^{-14}\, e^{-4500/RT},$$
$$k_1 = 1.3 \times 10^{-5}\, Z\, e^{-4100/RT}.$$

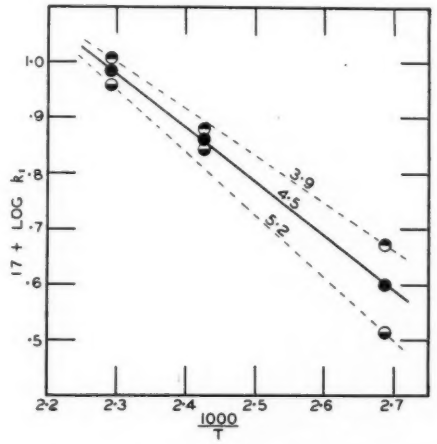

FIG. 2. Arrhenius plot for k_1. ◒ k_1', assuming first order recombination of H atoms; ◓ k_1'', assuming second order recombination of H atoms; ● mean of k_1' and k_1''.

ACCURACY OF THE RESULTS

The present results differ somewhat from those quoted in the preliminary note (13), viz. $p_1 \backsim 10^{-4}$, $E_1 \backsim 6.6$ kcal. per mole. However, the original values were obtained on the basis of first order recombination of H atoms only,

and it can be seen from Fig. 2 that this leads to high values of E_1. The original values of k_1 were also in error to a slight extent because no allowance had been made for the change in pressure and flow rate on adding methane to the hydrogen stream.

In estimating the accuracy of the present results it is necessary to make a distinction between the accuracy of the actual rate constants, on the one hand, and the accuracy of p_1 and E_1 on the other. We believe it unlikely that the value of k_1 for any temperature will be in error by more than a factor of two from any or all of the following causes: (*a*) errors in measurement, which are relatively small, (*b*) uncertainty in making the correction for H atom recombination, (*c*) neglect of reactions [3] and [4].

Neglect of reaction [3] could, at the most, cause an error of a factor of two in k_1, and this would require that all of the methyl radicals formed in [1] be used up in [3]; the small amount of ethane formed makes this unlikely. Some justification for eliminating reaction [4] from the present scheme is obtained from the data of Whittle and Steacie (25). For the lowest temperature quoted in their work, 210°C., they obtained the value $k_4/k_3^{1/2} = 22 \times 10^{-13}$, or, in terms of actual reaction rates, $R_4/R_3^{1/2} = 22 \times 10^{-13}(H_2)$. It follows that at 163°C., the highest temperature used in the present work,

$$R_4/R_3^{1/2} < 22 \times 10^{-13}(H_2),$$

and hence

$$R_4/R_1 < \frac{22 \times 10^{-13}(H_2)}{k_1(H)(CH_4)} R_3^{\frac{1}{2}}.$$

However, we have found that $R_3 < R_1$, and hence, using the data for experiment 7Md and assuming the average value of (H) to be one tenth of the initial value,

$$R_4/R_1 << \frac{22 \times 10^{-13}(H_2)}{\{k_1(H)(CH_4)\}^{\frac{1}{2}}} << 1.6 \times 10^{-2}.$$

It therefore seems justifiable to neglect reaction [4] in the present experiments.

Probably the greatest source of error in the determination of k_1 is in making the correction for H atom recombination. This error will be greatest at low temperatures, since recombination will then account for a greater proportion of the H atoms consumed; this is seen from Table I and Fig. 2.

A conservative estimate of the possible error in E_1 can be made by assuming an error of half the difference between k_1' and k_1'' for the highest and lowest temperatures used; this works out to be ± 1.2 kcal. per mole. The corresponding error in the exponent of A_1 in the expression $k_1 = A_1 e^{-E_1/RT}$ or of p_1 in the expression $k_1 = p_1 Z\, e^{-E_1/RT}$ is approximately 0.7. The actual errors in E_1, A_1, and p_1 may be somewhat greater.

DISCUSSION

The activation energy obtained in this investigation is considerably lower than previous estimates (18, 19). It is therefore appropriate to discuss at some length the methods and conclusions of previous investigators.

Bonhoeffer and Harteck (4), v. Wartenberg and Schultze (24), and Chadwell and Titani (5), using the discharge tube method, found no evidence of products at room temperature, and Geib and Harteck (11) found none at temperatures up to 183°C. These negative results were taken to indicate that k_1 was too small to measure, since no ethane appeared to have been formed by the combination of methyl radicals. However, we have found in the present work that the rate of ethane formation at low pressures is very much less than the rate of reaction [1]. Furthermore, the present data and those for ethane (2) show that at, say, 183°C. k_1 would be approximately equal to 0.04 k_5,

$$H + C_2H_6 = C_2H_5 + H_2, \qquad [5]$$

and hence for conditions which would lead to the measurable decomposition of hydrocarbons such as ethane, the amount of ethane produced from the methane reaction would be too small to measure. The present results are therefore not in disagreement with those obtained by the earlier workers.

Under certain conditions the use of D atoms affords a sensitive test for the occurrence of reaction [1], or more correctly reaction [1*a*],

$$D + CH_4 = CH_3 + HD. \qquad [1a]$$

This method has been used in the more recent work, but it will be seen from a detailed examination of the various papers that the authors have been reluctant to accept an interpretation of their data which would indicate a low value for E_{1a}.

Geib and Steacie (12) studied the reaction of D atoms with methane at 20° and at 100°C. by the discharge tube method. The amount of methane exchanged ranged from zero to 4.3%, but there appeared to be no correlation between the per cent exchange and the temperature. They attributed the apparent lack of reaction to E_{1a} being at least 11 kcal. per mole, taking the steric factor to be 0.1. It is significant that for a temperature of 100°C. this estimate corresponds to an activation energy of 4.1 kcal. per mole combined with a steric factor of 10^{-5}. In a similar investigation Steacie and Phillips (20) reported 1.9% exchange, in essential agreement with the results of Geib and Steacie.

Steacie (17) used the discharge tube method to investigate the reaction of D atoms with methane up to 500°C. The per cent exchange was corrected for what appeared to be exchange resulting from back diffusion of methane into the discharge. The correction was made by subtracting the average exchange at room temperature (4.3%) from all the values for higher temperatures. It seems not unreasonable to suppose that the small temperature coefficient of exchange at low temperatures might, at least in part, be attributed to reactions [1*a*] and [2*a*].

$$D + CH_3 (+ M) = CH_3D (+ M) \qquad [2a]$$

At the higher temperatures the rate of exchange would increase more rapidly by reason of reaction [4*a*], which would regenerate D atoms.

$$CH_3 + D_2 = CH_3D + D \qquad [4a]$$

The most recent value of E_{4a}, 11.8 kcal. per mole (25), is in line with this suggestion.

Trenner, Morikawa, and Taylor (22), also using the discharge tube method, reported no exchange of methane below 310°C. under conditions similar to

those in which the reaction of D atoms with ethane caused 24.2% of the latter to be consumed. However the present value of k_1 at, say, 163°C. is less than 1/20 of the value of k_5, and hence the amount of exchange to be expected would only be of the order of one per cent; this was close to the limit of error of the method used to determine C–D bonds.

While the present method involves, essentially, the measurement of the rate of exchange of methane without the use of D atoms, the actual rate of consumption of H atoms is a much more sensitive measure of the rate of [1] or [1*a*] than would be the determination of the per cent exchange. For example, it can be calculated that at 163°C. the per cent of methane exchanged in experiment 7Md would have been only 0.85.

Morikawa, Benedict, and Taylor (14) studied the $Hg(^3P_1)$ photosensitized exchange between D_2 and CH_4 over the temperature range 98° to 488°C. From 98° to 196°C. the temperature coefficient was very small; at the higher temperatures it corresponded to an activation energy of 12 kcal. per mole. They attributed the low-temperature activation energy of 4.5 kcal. per mole to the reaction

$$Hg(^3P_1) + CH_4 = CH_3 + H + Hg(^1S_0) \qquad [6]$$

rather than to reaction [1*a*].

This appears to be the only case in which an appreciable activation energy has been assigned to the dissociative quenching of a hydrocarbon. However their interpretation can only be made by disregarding the published quenching data for CH_4 and/or D_2 (1, 9). Taking into account the molecular weights of the two gases, these data predict that the quenching efficiency of D_2 should be almost 250 times that of CH_4. The maximum quantum yield for exchange through reaction [6] would then be only 0.004 at 98°C. The observed quantum yields at 98° were 0.42, 0.59, and 0.25. The predicted quantum yield could be raised to a maximum of 0.016 by postulating exchanges of the type

$$D + CH_3 = CH_2D + H \qquad [7]$$

but this would mean that most of the exchanged methane would be in the form of CD_4, contrary to their observations. If the low-temperature activation energy is assigned to reaction [1*a*] then the results of Morikawa, Benedict, and Taylor are in good agreement with the present results.

Darwent and Roberts (7) have pointed out what would appear to be an inconsistency between our results on reaction [5] (2) and our preliminary results on reaction [1] (13). Their work was based on the following mechanism:

$$D_2S + h\nu = D + DS, \qquad [8]$$
$$D + CH_4 = CH_3 + HD, \qquad [1a]$$
$$D + C_2H_6 = C_2H_5 + HD, \qquad [5a]$$
$$D + D_2S = D_2 + DS. \qquad [9]$$

The method consisted in measuring the ratio $(HD)/(D_2)$; with methane this should be proportional to $(CH_4)/(D_2S)$ with slope k_{1a}/k_9, with ethane it should be proportional to $(C_2H_6)/(D_2S)$ with slope k_{5a}/k_9. The determination of

activation energies of reactions such as [1*a*] or [5*a*] by this method requires the determination of the effect of temperature on these slopes, and a knowledge of E_9 (and the steric factor p_9, if steric factors are to be calculated as well). The difference in activation energy for reaction [10],

$$D + H_2 = H + HD, \qquad [10]$$

and reaction [9] was evaluated from the effect of temperature on the slope of the $(HD)/(D_2)$ vs. $(H_2)/(D_2S)$ curve for experiments in which H_2 was substituted for the hydrocarbon. E_9 (as well as p_9) was calculated by adopting the values $E_{10} = 5$ kcal. per mole, $p_{10} = 0.07$ (6). These latter values have recently been questioned (3), and hence the most reliable method of comparing our results with those of Darwent and Roberts would seem to be in terms of rate constants, rather than activation energies.

At 400°C. Darwent and Roberts found a considerable increase in $(HD)/(D_2)$ for an increase in $(C_2H_6)/(D_2S)$, but not for an increase in $(CH_4)/(D_2S)$. However, on the basis of our present results the slope of the latter curve would be only about 1/35 of that for ethane. The values of $(HD)/(D_2)$ would therefore not be expected to rise much above the "background" value of 0.25, to which all of their curves extrapolated (although according to theory all of the curves should extrapolate to zero).

Space does not permit further consideration of the results of other workers on reactions [1] and [1*a*]. The earlier literature has been covered by Steacie (18).

Although more reliance can be placed on the values of k_1 than on the calculated values of E_1, it is of interest to compare our value of E_1 with bond dissociation energy data. The C–H bond dissociation energy in methane has been estimated to be 102 ±1 kcal. per mole (21), although the temperature to which this value applies is not certain. The dissociation energy of H_2 at 25°C. is 104.2 kcal. per mole (15). It is probably safe to assume that the change in internal energy for reaction [1] is approximately 2.2 ± 1 at temperatures of the order of 150° to 200°C. Whittle and Steacie (25) quote a value of 10.0 kcal. per mole for E_4. Since we have found E_1 to be 4.5 kcal. per mole, there would appear to be a noticeable discrepancy in the results in so far as agreement with the relation

$$E_4 - E_1 = -\Delta E^0 \qquad \text{(viii)}$$

is concerned. However, taking into consideration the uncertainty in each of the activation energy values, the uncertainty in $-\Delta E^0$, and the uncertainty in the validity of (viii) as applied to activation energies calculated in a particular way, the discrepancy may be more apparent than real.

ENTROPY OF THE METHYL RADICAL

More rigorous than (viii) is the relation

$$RT \ln (k_1/k_4) = T\,\Delta S^0 - \Delta E^0, \qquad \text{(ix)}$$

from which it is possible to calculate ΔS^0 at any temperature for which values of k_1, k_4, and $-\Delta E^0$ are known. The largest source of error is probably in the

last quantity. Unfortunately the temperature ranges for our data and those of Whittle and Steacie do not overlap, but a negligible error should arise in extrapolating the latter data to 163°C., at which temperature k_1 is 9.62×10^{-17}. Whittle and Steacie obtained data for $k_4/k_3^{1/2}$, rather than for k_4. They found $p_4/p_3^{1/2}$ to be 1.6×10^{-3} and $E_4 - \frac{1}{2}E_3$ to be 10.0 kcal. per mole, but since p_3 is undoubtedly in the range 0.01 to 1.0, and E_3 is approximately equal to zero, the value of k_4 at 163°C. can be estimated with some certainty to be in the range 1.08×10^{-18} to 1.08×10^{-17}. Assuming, as before, that $-\Delta E^0 = 2.2 \pm 1$ kcal. per mole, it can be shown that $\Delta S^0 = 1.6 \pm 4.6$ e.u. From thermodynamic data for H, CH_4, and H_2 (15) it follows that S^0 for the free methyl radical is 44.9 ± 4.6 e.u. at 163°C.

Extrapolation of the data of Whittle and Steacie to 99°C., the lowest temperature used in the present experiments, yields the value 45.3 ± 5.0 e.u. for the entropy of the methyl radical at that temperature. If the present data on reaction [1] are extrapolated to 210°C., the lowest temperature quoted by Whittle and Steacie, using the values $A_1 = 1.7 \times 10^{-14}$, $E_1 = 4.5$ kcal. per mole, the entropy of the methyl radical at that temperature is found to be 49.3 ± 4.4 e.u. A higher value at this temperature is to be expected on thermodynamic grounds.

Some years ago Zeise (26) calculated the entropy of the methyl radical to be 47.345 at 298°K., 49.80 at 400°K. The values calculated from kinetic data on reactions [1] and [4] are in satisfactory agreement. Trotman-Dickenson (23) has recently estimated a value of 45.5 e.u. at room temperature.

Trotman-Dickenson (23) has utilized the equation

$$R \ln (A_1/A_4) = \Delta S \qquad \text{(x)}$$

to calculate ΔS, but this procedure is less reliable than the use of (ix) because of the assumptions of a theoretical nature involved, and because errors in A and E are complementary.

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STRESSES AND STRAINS IN ADSORBENT–ADSORBATE SYSTEMS[1]

By E. A. Flood and R. D. Heyding[2]

ABSTRACT

From thermodynamic considerations a simple equation is derived which correlates length changes of a porous rigid adsorbent with its elastic and adsorptive properties. The equation contains a structure factor which is a constant characteristic of the adsorbent. Calculated and observed results agree reasonably well and suggest that, in the cases concerned, the assumptions underlying the derivation of the equation are valid. The underlying assumptions are: (*a*) both adsorbate and adsorbent can each exist separately in equilibrium with externally applied forces in states that are thermodynamically identical with their states in the adsorbate–adsorbent system, (*b*) adsorption isotherms represent paths of thermodynamic reversibility.

INTRODUCTION

In previous papers we have shown that the pore dimensions of both micropore and macropore systems of certain activated carbons may be estimated from permeability data (7). The dimensions of the micropore systems were related to micropore permeability by means of equations derived from the thermodynamic conditions for equilibria of single component fluids in potential fields. Thus micropore permeability equations were based upon the assumption that, in the adsorption reaction, the adsorbate and adsorbent retain their own individual properties.

This paper is mainly concerned with stress–strain inferences derivable from this assumption, as well as with the plausibility and limitations of the assumption. More particularly, the basic assumption is: Assemblies of volumes of the pure adsorbable gas and assemblies of volumes of the pure adsorbent can each exist separately, in equilibrium with externally applied forces, in states that are thermodynamically identical with their states in the adsorbent–adsorbate system. When and only when this assumption holds, is it theoretically possible to determine the change in the state of stress of the adsorbent resulting from the adsorption reaction, and to correlate this change in state of stress with the elastic constants of the pure adsorbent and with its dimensional changes.

When this assumption is applied to an isotropic porous adsorbent the following very simple equation (Equation 16) can be deduced:

$$\delta l/l = -\tfrac{1}{3}\beta(1 + \phi K - \phi K\alpha)\delta p.^{3}$$

This equation thus provides a basis for a fairly sensitive experimental test of the validity of the assumption that in the adsorption reaction the adsorbate

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[2] *National Research Council Postdoctoral Fellow, 1951–53.*

[3] *$\delta l/l$ = length change per unit length; β = coefficient of cubical compressibility of the solid adsorbent; ϕ = ratio of void volume to solid volume; K = ratio of linear average stress to volumetric average stress; α = mean number of volumes adsorbed averaged over the pressure interval δp; p = hydrostatic pressure of fluid surrounding the adsorbent–adsorbate system.*

and adsorbent retain their own individual properties. Accordingly, some experiments have been carried out, the results of which suggest that this assumption is reasonably valid as applied to large adsorptions by certain activated carbons.

It may be remarked that Hill (10) has pointed out some of the difficulties in distinguishing clearly between the thermodynamics of adsorption processes which are essentially "solution" processes and those special cases which are in conformity with the above assumptions.

In what follows, a simple theoretical development of some inferences derivable from the above assumption is presented, together with some experimental results and relevant discussion.

THEORETICAL

For a process of transformation of two separate systems into a single system containing the same matter where the temperatures, pressures, surface tensions, etc. of the systems are to remain constant during the process, the condition that it shall be reversible is,

$$F_1 + F_2 = F_{12}, \qquad [1]$$

where F_1, F_2, and F_{12} are the free energies[4] of the first, second, and combined systems, respectively. Accordingly, in order that the process of transformation of the separate systems into the combined system shall remain reversible at any point along a path of variation of the three systems, the path of variation is subject to the condition,

$$dF_1 + dF_2 = dF_{12}. \qquad [2]$$

Applying this equation to the isothermal reaction between a gas and an almost incompressible solid of very low vapor pressure, p_{2s}, which forms a solid product under a hydrostatic pressure very nearly equal to that of the pure gas with which it is in equilibrium, that is, applying Equation 2 to conditions analogous to those which prevail during gas adsorption measurements, we can write,

$$v_1 dp_1 + dF_2 = v_{12} dp_{12}, \qquad [3]$$

where v_1 is the volume of the pure gas at the equilibrium pressure, p_1, corresponding to the mass, n_1, of gas adsorbed and v_{12} is the volume of the combined system whose hydrostatic pressure is p_{12}.

Equation 3 thus describes a point of the path of variation for changes in the pressures p_1 and p_{12} along which $\Delta F = 0$ for the process of transformation of the pure components into the combined system. Integrating Equation 3 between appropriate limits we can describe the path of variation, corresponding to a constant mass of sold, n_2, interacting with any quantity of gas, n_1, and thus obtain,

$$\int_{p_1=0(n_1=0)}^{p_1=p_1(n_1=n_1)} v_1 dp_1 + \int_{p_{2s}(n_2)}^{p_2(n_2)} dF_2 = \int_{p_{2s}(n_1=0,n_2=n_2)}^{p_{12}(n_1=n_1,n_2=n_2)} v_{12} dp_{12}. \qquad [4]$$

[4] $F = E = -TS + pv + \gamma\Sigma$, *where* E = *energy*, S = *entropy*, γ = *surface tension*, Σ = *surface area, etc.*

Since p_{2s} is assumed very low, $p_{12} \approx p_1$, accordingly, we can write,

$$[5] \qquad \Delta F_2 = \int_{p_{2s}}^{p_1} v_{12} dp_{12} - \int_0^{p_1} v_1 dp_1 = \bar{v}_{12} \cdot p_1 - \bar{v}_1 \cdot p_1$$

where $\bar{v}_1$ is defined by $\bar{v}_1 \cdot p_1 \equiv \int_0^{p_1} v_1 dp_1$ and $\bar{v}_{12}$ is similarly defined.

In the case of large adsorptions, $\bar{v}_1$ will be, in general, much larger than $\bar{v}_{12}$, the latter being of the order of the volume of the solid. Hence for large adsorptions we can neglect $\bar{v}_{12} \cdot p_1$ in comparison with $\bar{v}_1 \cdot p_1$ and assuming the gas ideal over the given pressure range, we can write,

$$[6] \qquad \Delta F_2 = -\int_0^{p_1} v_1 dp_1 = -\frac{RT}{Mv_0} \int_0^{p_1} \frac{v_0'}{p_1} dp_1,$$

where v_0' is the volume of gas adsorbed expressed as cc. reduced to N.T.P., p_1 is the equilibrium gas pressure, and v_0 is the volume per mole of adsorbate at N.T.P. Free energy per gram, F_2.

ΔF_2, as given in Equation 6, is the change in free energy of pure adsorbent when changed from its initial state under its own vapor pressure to its combining state. Thus for a given mass of a particular solid and gas at a given temperature, ΔF_2 is usually a function of p_1 alone and is uniquely determined by the observed value of the integral $\int_0^{p_1} v_1 dp_1$ provided that the observed integral represents an integral along the path of thermodynamic reversibility corresponding to minimum free energies of the combined systems. ΔF_2 may be expressed in a number of more or less arbitrary ways. Thus we may suppose the solid of volume v_c to be subjected to a change in hydrostatic pressure Δp_c or we may suppose that the solid of surface area Σ has undergone a change in surface tension, $\Delta\gamma$, and thus write $\Delta F_2 = \bar{v}_c \cdot \Delta p_c$ or $\Delta F_2 = \bar{\Sigma} \cdot \Delta\gamma$ according as we prefer to suppose that the change in potential of the solid is mainly due to a change in its volume free energy or in its surface free energy. Hence we may write,

$$[7] \qquad \bar{v}_c \cdot \Delta p_c = \bar{\Sigma} \cdot \Delta\gamma = -\frac{RT}{Mv_0} \int_0^{p_1} \frac{v_0'}{p_1} dp_1,$$

which is the equation commonly used (8, 9) in discussing these problems.

If we now suppose that $\bar{v}_c \cdot \Delta p_c$ or $\bar{\Sigma} \cdot \Delta\gamma$ refers *not only* to the combining state of the pure adsorbent separately, but actually describes its condition exactly in the mixed system we can attempt to correlate the values of $\bar{v} \cdot \Delta p_c$ and/or $\bar{\Sigma} \cdot \Delta\gamma$ to the dimensional changes of the adsorbent–adsorbate system and to the elastic constants of the pure solid. Both Δp_c and $\Delta\gamma$ are measures of changes in states of stress and since the solid is almost incompressible, its elastic constants will be much the same in the stressed and unstressed states.

Equations of the form of Equation 7 have been used with considerable success by a number of investigators (1, 2, 3, 4, 8, 9) to correlate dimensional changes, resulting from adsorption, with calculated "spreading pressures" and with the compressibilities of various adsorbent materials. Thus there appears to be some validity in the supposition that in these cases $v_c \cdot \Delta p_c$ or $\bar{\Sigma} \cdot \Delta\gamma$ refers not only to the state of stress of the pure adsorbent separately but refers, as well, to its state in the mixed system. This supposition is equivalent to the assumption that the combined system consists of two pure substances which exert mechanical or similar forces upon one another while each substance retains its original equation of state. In order to bring out more clearly the physical nature of this very important assumption, as well as to indicate something as to its plausibility and limitations, it seems worth while to look into the problem in a little more detail.

In Equations 3 and 4, v_{12} represents the total volume of the porous solid. This volume consists of the sum of the volumes of solid and void space, namely, the sum of the volumes v_c and v_a, respectively.

It is, accordingly, convenient to rewrite Equation 4 in the form

$$[8] \qquad \int_0^{p_a} v_a dp_a + \int_{p_{2s}}^{p_c} v_c dp_c = \int_{p_{2s}}^{p_1} v_{12} dp_{12},$$

where $v_{12} = v_a + v_c$, and p_a is the pressure of the pure adsorbate in a volume v_a. p_c and v_c represent the pressures and volume of the solid, respectively, and p_1 is the pressure of the gas surrounding v_{12}, i.e., the equilibrium pressure and also the hydrostatic pressure of the combined system.[5]

Equation 8 is subject to the condition,

$$[9] \qquad \int_0^{p_1} v_1 dp_1 = \int_0^{p_a} v_a dp_a.$$

Thus the volume v_a is separated from v_1 by the potential energy difference $\int_{p_1}^{p_a} v dp$.

Equation 8 is valid for any type of equilibrium since the integrals on the left are more or less arbitrary expressions of the free energy changes of the pure components from specified initial states. In the case of a two component chemical compound or in the case of a two component solution, no very definite meaning can be given to "v_a" and "v_c", the volumes of the components in the compound or in the solution, while in the case of mechanical mixtures, these volumes are quite definite. The assumption that the mixed system consists literally in the mechanical combination of the two separate systems or assemblies of systems of pure substances without change of their volumes or their forms, pressures, entropies, or any of their properties except their positions with respect to

[5] *If we prefer to regard the solid in its initial state as existing under a condition of stress corresponding to, say, p_c', we can add the integral $\int_{p_c'}^{p_{2s}} v_c dp_c$ to both sides of Equation 8.*

one another, distinguishes this special case of "reaction" from the more general type of reaction where there are various heat and other effects accompanying the equilibrium conversion of the separate systems into the combined system. In the latter more general type of reaction, neither of the separate systems can exist in a state or assembly of states in equilibrium with externally applied forces that shall be identical with their states in the combined system. In the special type of reaction which we are considering, the volume v_a in the adsorbent is to be regarded as containing the same substance as the equilibrium gas, and the equilibrium conditions as between the adsorbate in v_a and the gas in equilibrium therewith as resembling the equilibrium conditions which persist between two volumes of gas at different heights in a gravitational field. While the potential difference separating the two volumes in the latter case is a constant and independent of the temperature and pressure and of the nature of the gas, in the former case, although the potential difference between the volumes v_a and v_1 is constant during the transformation of the separate systems into the combined system, in general, this potential difference is dependent upon p_1 and upon the temperature and upon the natures of the gas and solid. Under these conditions, in order that an equilibrium exist at constant temperature as between the gas outside of v_a and that within v_a, as we vary the pressure, p_1, of the gas outside, we must have $v_a dp_a = v_1 dp_1$, hence,

$$[10] \qquad p_a = \int_0^{p_1} \frac{\rho_a}{\rho_1}\, dp_1,$$

where ρ_a is the mean density of the substance in v_a and ρ_1 is the density of the gas.

If within the volume v_a the densities vary, the equation is still valid, p_a representing the volumetric average pressure. Thus consider v_a made up of the sum of the small volumes v_i, where in each elementary volume v_i the density can be regarded as uniform. Then for each small volume we may write

$$[10a] \qquad p_{ai} = \frac{1}{v_i}\int_0^{p_1} \frac{m_i}{\rho_1}\, dp_1,$$

where m_i is the mass of material in the constant elementary volume v_i and $m_i/v_i = \rho_{ai}$. Thus we obtain

$$\sum v_i p_{ai} = \int_0^{p_1} \frac{\sum m_i}{\rho_1}\, dp_1$$

and hence,

$$\frac{\sum v_i p_{ai}}{\sum v_i} = p_a = \frac{1}{v_a}\int_0^{p_1} \frac{\sum m_i}{\rho_1}\, dp_1 = \int_0^{p_1} \frac{\rho_a}{\rho_1}\, dp_1.$$

Since ρ_a/ρ_1 is inherently positive, the integral must be positive for increasing values of p_1. Accordingly, along a path of thermodynamic reversibility p_a cannot become negative as p_1 increases. However, if at some point along the path of $\int_0^{p_1} v_1 dp_1$, a phase change occurs so that a second path of reversible

variation[6] intersects the path of increasing pressure at some point, say, p_1', then as the equilibrium pressure is reduced from p_1', the system may pass along the second path and p_a will be given by,

$$[11] \qquad p_a = \int_0^{p_1'} \frac{\rho_a}{\rho_1}\, dp_1 + \int_{p_1'}^{p_1} \frac{\rho_a'}{\rho_1}\, dp_1.$$

Thus p_a may become negative if the second integral is larger than the first. For example, if the volume, v_a, is filled with liquid at p_1' and the pressure is then reduced, the liquid may persist and the value of ρ_a'/ρ_1 exceeding ρ_a/ρ_1, p_a may become negative.

Since the volumes v_a, v_c, and v_{12} are practically constant we can write Equation 8 in the form

$$[12] \qquad v_a \cdot p_a + v_c \cdot p_c = v_{12} \cdot p_1 = (v_a + v_c)p_1.$$

If the volumes v_a and v_c are made up of regions under varying stresses, it is to be understood that p_a and p_c are volumetric averages, i.e.,

$$v_{ai}p_{ai} + v_{ci}p_{ci} = (v_{ai} + v_{ci})p_1,$$

and

$$\sum v_{ai}p_{ai} + \sum v_{ci}p_{ci} = (v_a + v_c)p_1,$$

hence, in Equation 12,

$$p_a = \sum v_{ai}p_{ai}/\sum v_{ai} \text{ and } p_c = \sum v_{ci}p_{ci}/\sum v_{ci}.$$

Thus we can write

$$p_c = p_1 + (v_a/v_c)p_1 - (v_a/v_c)p_a,$$

and since

$$p_a = \int_0^{p_1} \rho_a/\rho_1 \cdot dp_1 = (\overline{\rho_a/\rho_1}) \cdot p_1 = \alpha p_1,$$

defining α, and putting $v_a/v_c = \phi$, we get the very simple basic equation

$$[13] \qquad p_c = (1 + \phi - \phi\alpha)p_1.$$

Equation 13 gives the average volumetric change in pressure or stress of the solid adsorbent from its state of stress where the adsorbable gas pressure is zero, to its state of stress when in equilibrium with the gas whose pressure is p_1.

[6] *In general this second path of reversible variation is not one for which the free energy of the whole system is a minimum for given values of the potential of the adsorbate and given quantities of adsorbent. If the state of the system "jumps" from one of these paths to the other, the process is thermodynamically irreversible.*

The formation of surfaces of tension within a given volume, along a path where the equilibrium pressure increases from zero, will, in general, render observed values of $\int_0^{p_1} v_1 dp_1$ *an inexact measure of* ΔF_1. *Once a surface is formed, changes in the area and form of the surface may be perfectly reversible. Under these conditions,* $\Delta F_1'$ *is measured by the observed values of* $\int_{p_1}^{p_1'} v_1 dp_1$, *and the pressure changes within the system containing the interface are given by*

$$\Delta p_a = \int_{p_1}^{p_1'} \rho_a/\rho_1 \cdot dp_1.$$

Where hysteresis occurs, whether due to the mechanism usually implied by the term "capillary condensation" or to such a mechanism as proposed by Pierce and Smith (11), or to any other mechanism consistent with our basic assumptions, the above considerations are equally applicable.

If we wish to correlate length changes with the changes in stress resulting from adsorption we introduce Hooke's Law and assuming isotropy, we can write

$$\delta v/v = 3\delta l/l = -\beta\delta p$$

where v is the volume of the porous solid, l its length, β the compressibility, and p the uniform state of stress or pressure. If the pressures are not uniform along the length l, we must write

[14] $$\delta l/l = -\tfrac{1}{3}\beta \sum l_i \delta p_i / \sum l_i = -\tfrac{1}{3}\beta\overline{\delta p}$$

where $\overline{\delta p}$ is the change in linear average state of stress. In general, the linear average stress of linear average pressure will differ by a more or less constant factor from the volumetric average pressure unless the pressures are practically uniform. If the pressures on the solid adsorbent are uniform, we can write

[15] $$\delta l/l = \tfrac{1}{3}\beta(1 + \phi - \phi\alpha)\delta p_1$$

where the symbols are as indicated previously. α is the mean value of ρ_a/ρ_1(i.e. the mean value of the number of volumes adsorbed) averaged over the pressure interval δp_1.[7] Where the solid pressures are not constant, we must write

[16] $$\delta l/l = \tfrac{1}{3}\beta(1 + \phi K - \phi K\alpha)\delta p_1$$

where K is a small numerical factor dependent upon the structure of the porous solid and upon more detailed considerations which we shall discuss later with reference to particular models (cf. Appendix II). In general, ϕK should be more or less independent of the nature of the adsorbate, but a characteristic of the structure of the adsorbent and the nature of the surface forces involved in adsorption; K may thus be regarded as a structure factor.

If the porous rod is immersed in an incompressible liquid which fills the void space completely and the pressure of the surrounding liquid is increased by δp_1 the value of α will be unity over this pressure range and Equation 16 reduces to,

$$\delta l/l = -\tfrac{1}{3}\beta\delta p_1,$$

which should therefore apply approximately to the case where the rod is immersed in liquid water. For no adsorption, i.e., $\alpha = 1$, the equation also reduces to the above simple form, as of course it should. For large adsorptions, i.e., $\alpha \gg 1$, the equation becomes,

[16a] $$\delta l/l = \tfrac{1}{3}\beta\phi K\alpha\delta p_1 = \tfrac{1}{3}\beta\phi K\delta p_a,$$

and hence $\delta l/l$ becomes proportional to $\int_0^{p_1} \rho_a/\rho_1 \cdot dp_1$, and where the equilibrium gas is ideal, $\delta l/l$ is proportional to $\int_0^{p_1} v_0' \, d(\log p_1)$ and hence, where the quantity adsorbed is comparatively constant, $\delta l/l$ becomes proportional to $\log p_1'/p_1$ over the interval p_1 to p_1', as found by Amberg and McIntosh (1).

It is to be emphasized that Equation 16 is valid for any type[8] of adsorption by any virtually incompressible solid provided that the adsorbate (and hence

[7] *The calculation of p_a from isotherm data according to Equation 10 is very simple. From the isotherm, values of ρ_a/ρ_1 are calculated and plotted against p_1, the equilibrium gas pressure. p_a is the area under the curve from 0 to p_1. In the case of hysteresis loops p_a is the difference of the areas under the curve from 0 to p_1' and the area under the curve p_1' back to p_1, preferably along the "scanning curve".*

[8] *Any shape of adsorption isotherm can be consistent with Equation 16.*

also the adsorbent) behaves as a single pure substance and also provided that no irreversible processes occur, i.e., provided $\int_0^{p_1} v_1 dp_1$ does in fact measure ΔF_1.

CALCULATED AND OBSERVED EXTENSIONS

As a test of the validity of these assumptions as applied to real systems, we have made use of some published data to compare observed extensions with those calculated by means of Equation 16*a*.

In Figs. 1, 2, and 3 calculated extensions are compared with those obtained experimentally by Haines and McIntosh (8) for activated carbon rods. The numerical value of βK is chosen to make the equation fit the observed result for saturated water vapor. The same value of βK is used for dimethyl ether and for ethyl chloride. It will be noted that βK is somewhat greater than the compressibility of graphite. In Fig. 4 calculated values are compared with those obtained experimentally by Wiig and Juhola (12) for a long column of short carbon rods placed end to end, while in Fig. 5 calculated extensions are compared with the precise extension measurements of Amberg and McIntosh (1) using porous glass rods, the value of βK again being taken so as to fit the extension at saturation. Evidently Equation 16*a* fits these data as well as could be expected since (*a*) none of the samples were known to be isotropic, (*b*) in the data of Haines and McIntosh the adsorption isotherm for water refers to a different sample from that used to measure extensions, (*c*) in Wiig

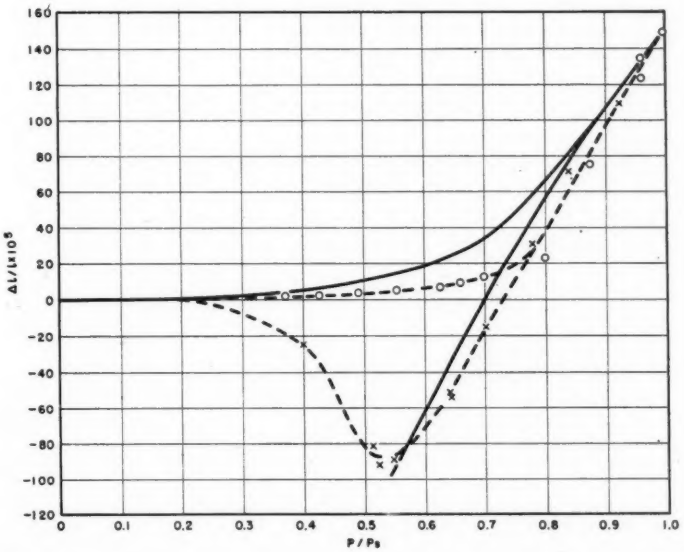


FIG. 1. Adsorption extension: Water vapor on carbon (data of McIntosh and Haines). Broken line drawn through experimental points. ○, Adsorption; ×, Desorption. Solid line calculated from: $\delta l/l = + \frac{1}{3}\beta\phi K\alpha p_1 = 3.43 \cdot 10^{-7} \cdot \alpha p_1$.($\beta K = 4.76 \cdot 10^{-7}$/p.s.i.; $\phi = 2.16$.)

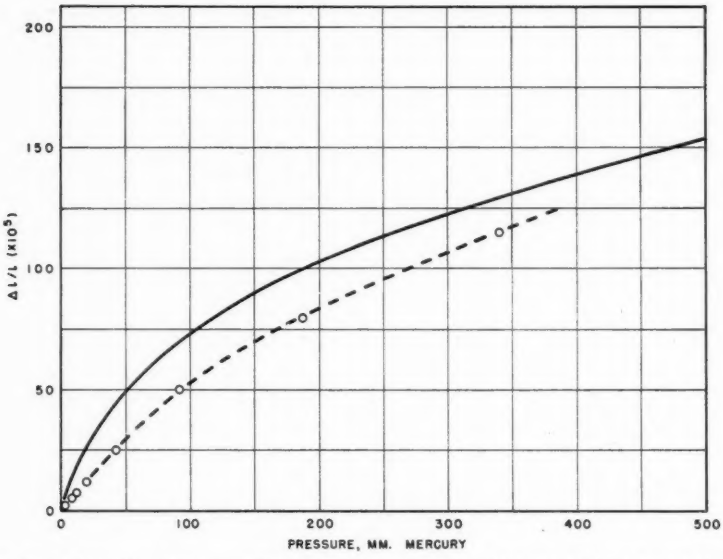


FIG. 2. Adsorption extension: Dimethyl ether on carbon (data of McIntosh and Haines). Broken line drawn through experimental points. Solid line calculated from: $\delta l/l = 3.43 \cdot 10^{-7} \cdot \alpha p_1$.

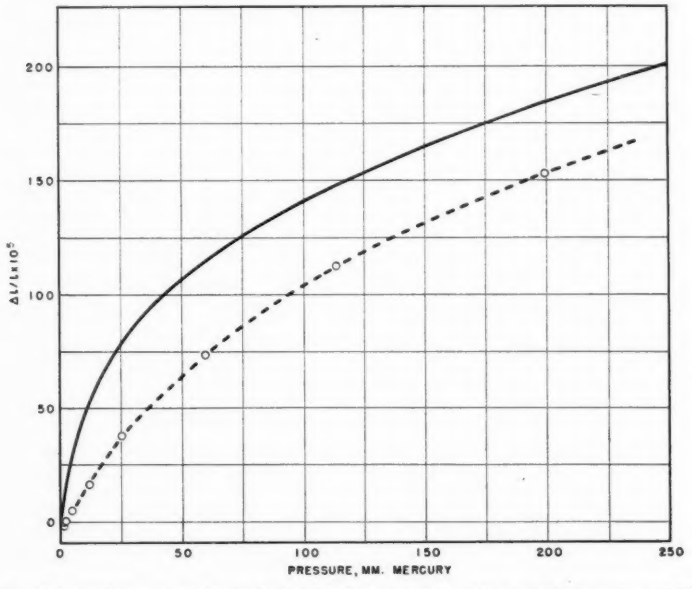


FIG. 3. Adsorption extension: Ethyl chloride on carbon. (data of McIntosh and Haines). Broken line drawn through experimental points. Solid line calculated from $\delta l/l = 3.43 \cdot 10^{-7} \cdot \alpha p_1$.

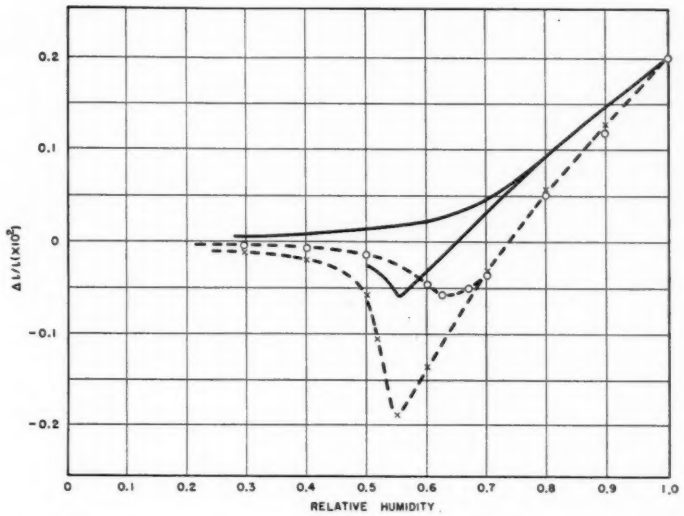


FIG. 4. Adsorption extension: Water vapor on carbon (data of Wiig and Juhola). Broken line drawn through experimental points. ○, Adsorption, ×, Desorption. Solid line calculated from: $\delta l/l = + \frac{1}{3}\beta K\phi\alpha p_1 = 3.49 \cdot 10^{-7} \cdot \alpha p_1$. ($\beta K = 6.54 \cdot 10^{-7}$/p.s.i.; $\phi = 1.60$.)

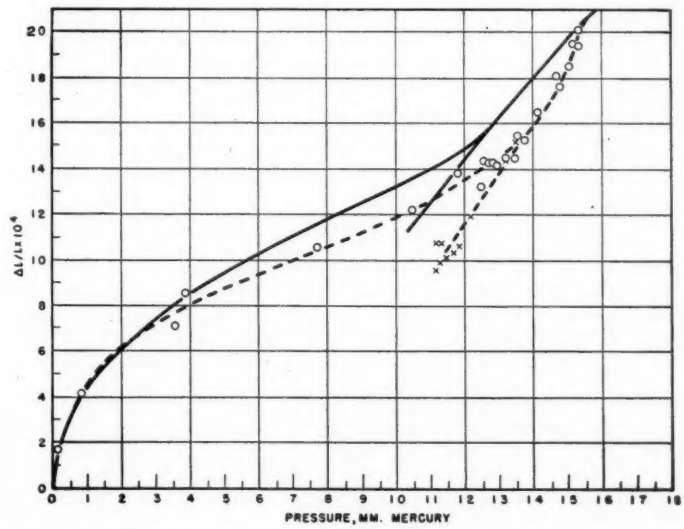


FIG. 5. Adsorption extension: Water vapor on porous glass (data of Amberg and McIntosh). Broken line drawn through experimental points. ○, Adsorption; ×, Desorption. Solid line calculated from: $\delta l/l = + \frac{1}{3}\beta\phi K\alpha p_1 = 3.69 \cdot 10^{-7} \cdot \alpha p_1$. ($\beta K = 5.76 \cdot 10^{-7}$/p.s.i.; $\phi = 1.92$.)

and Juhola's experiments there was some lack of reproducibility of the data, and finally, (*d*) because of the high surface tension of liquid water, irreversible processes are apt to occur within the adsorbent and consequently $\int_0^{p_1} \rho_a/\rho_1 \cdot dp_1$ is apt to give an inaccurate measure of p_a.

As an additional check on the validity of Equation 16 we have made some measurements of the extensions in length of a long thin activated carbon rod, when exposed to various pressures of helium, nitrogen, water vapor, and liquid water at room temperature. Measurements of radial extensions of the same rod when exposed to water vapor have also been made. Relevant adsorption isotherms were determined and the values of β and ϕ and K determined from the data.

In general terms, the results obtained may be summarized as follows:

(*i*) No appreciable change in length of the rod could be detected as between its length when in equilibrium with water vapor very close to the saturation pressure and when immersed in liquid water.

(*ii*) When immersed in liquid water the length decreases with increasing pressure of the surrounding water. The mean compressibility (0–2000 p.s.i.) in liquid water is close to that of pure graphite (5) but shows a tendency to increase with increasing pressure. If liquid water does not fill the void space completely, the value of α will tend to increase as a result of forcing water into empty spaces, thus reducing the apparent compressibility. Further, since water is slightly compressible, the compressibility decreasing with increasing pressure, α will approach unity more closely the higher the pressure. Thus in both of these cases the apparent compressibility should increase with increasing pressure. Evidently the observed behavior is consistent with Equation 16.

(*iii*) In the case of helium, the length also decreases with increasing pressure up to 1600 p.s.i. However, the apparent mean compressibility is considerably less than that of graphite (about one half) suggesting some adsorption of helium (5–10%) and/or adsorption of traces of water vapor from the helium. The accuracy of the measurements was not sufficient to make any reliable estimate of the helium adsorption.

(*iv*) In the case of nitrogen, the rod increases in length as the pressure of the nitrogen is increased from 0 to 1600 p.s.i. The increases in length can be calculated with surprising accuracy by Equation 16, making use of the adsorption isotherm data. Even if K is taken as unity in Equation 16 and the apparent value of β taken from the extension of the rod in saturated water vapor the calculated extension in nitrogen at 1600 p.s.i. is within 10% of the observed value. It will be noted that in these two cases the numerical values of α are very different, being of the order of 3 for nitrogen and of the order of 10^4 in the case of saturated water vapor.

(*v*) When exposed to water vapor at low relative humidities, the rod contracts slightly ($\sim 0.03\%$), the contraction increasing with increasing pressure up to 10 to 11 mm. Hg, and subsequently expands considerably. The extension (0.36%) at saturation (23.65 mm. Hg) although agreeing fairly well with calculated values is too large to be quite consistent with those

obtained with nitrogen. The desorption behavior is practically identical with the adsorption behavior. (These carbon rods show comparatively little adsorption hysteresis.) Changes in diameters of the rod due to water vapor adsorption were found to be essentially similar to the changes in length.[9]

Details concerning experimental methods and materials are given in Appendix I, the experimental results being recorded in Figs. 6 to 9.

Evidently, Equation 16 describes the general extension behavior of the carbon rod very well but fails to describe the extensions when the carbon rods are exposed to water vapor at low relative humidities (cf. Wiig and Juhola's data). While this failure may be due to the system behaving as a two-component system or to rather bizarre structural effects, we believe that the failure of Equation 16 in this region is due to the irreversible formation of liquid-vapor menisci. While adsorption at a few isolated regions might easily give rise to a contraction in one direction and to expansions in directions perpendicular thereto, the net effect of the surface forces still corresponding to a net compression of adsorbate and extension of adsorbent, a net compression of adsorbate can hardly be consistent with contractions in both the length and diameter of the rod, i.e., it seems unlikely that non-isotropic solid tensions will give rise to contractions of the rod along its three principal axes. The contractions, when the rods are exposed to low relative humidities of water vapor, are thus considered to be due to the adsorbate having a net negative pressure—a condition consistent with reversible *desorption* paths *only*, i.e., paths involving some reduction in equilibrium pressure. Thus we believe that in these cases the isotherm of thermodynamic reversibility, the true measure of ΔF_1 and of $\int_0^{p_1} \rho_a/\rho_1 \cdot dp_1$, lies to the right of the observed isotherm (i.e. the isotherm ordinate, x/m, should be smaller for given equilibrium pressures).

Assuming the compressibility of the rod to be practically the same as that of graphite (5), i.e., taking 3.3×10^{-7}/p.s.i. as the value of β, and assuming 4.8 as the axial value of ϕK, all of our data are reasonably self-consistent as well as being consistent with what is to be expected in such cases. The calculated axial extensions in the cases of nitrogen, liquid water, and water vapor, Figs. 8 and 9, are based on these values of β and ϕK (cf. Appendix II).

DISCUSSION

Evidently the view that the adsorbate may be regarded as the same substance as the pure gas which it adsorbs is qualitatively in agreement with the facts in these cases. However, there are undoubtedly many other cases of "adsorption" where real bonds are formed between adsorbent and adsorbate and where a considerable fraction of the molecules of the adsorbed material are in energy states that are not attainable by molecules of either the adsorbate or adsorbent alone. Such a situation might be expected in the case of the highly specific catalytic activity of many adsorbing catalysts. However,

[9] *In view of these small initial contractions, the extension behavior of the rod on exposure to nitrogen was reexamined with considerable care especially in the low pressure region. No contractions could be detected.*

if the bonds of the adsorbent are very strong, the residual orbital fields and any Van der Waals or Lennard-Jones type forces might have little specific character and the resultant field within a narrow capillary space behave as an almost wholly nonquantized attractive force field of considerable range. In such a case any work done by the field would cause a change in the state of stress of the material that could be very closely paralleled by the application of external forces. However, if the surface is very large it seems very improbable that no regions are formed where the state of the adsorbate–adsorbent system is essentially a two-component system. The known effects of various adsorbates on the formation of surface complexes indicate that in activated charcoals there are undoubtedly regions which cannot be identical thermodynamically with two separate components in any pure state. However, in general, where large adsorptions occur in fine-grained rigid porous adsorbents there is a good deal of evidence that indicates that by far the larger part of the adsorbate may be regarded as a single substance. Thermodynamically, a clear distinction between chemisorption and physical adsorption can be made, if by physical adsorption we restrict the adsorption reactions to those where assemblies of the separate systems of adsorbate and adsorbent can each exist separately in equilibrium with externally applied forces in states which are identical thermodynamically with their states in the adsorbate–adsorbent system.

APPENDIX I—EXPERIMENTAL DETAILS

1. *Materials*

Activated Carbon Rods

Except where noted, all of the experiments were carried out with Carbon Rod No. 1. This rod was nearly straight, 88 mm. in length, and 1.78 mm. in diameter. Apparent (mercury) density, 0.753; helium density, 2.00; total void volume per cc., 0.623; micropore void volume (H_2O adsorption) per cc., 0.302; carbon volume per cc., 0.377.

The carbon rod used was one taken from a group of long straight rods supplied through the courtesy of the National Carbon Company. The rods are believed to have been made by extruding a zinc chloride – wood meal plastic mix to which had been added activated coconut shell charcoal fines. After extrusion and baking, these rods were remarkably straight but during the subsequent activation ($\sim$900°C.) considerable distortion occurred. However, a number of reasonably straight rods were selected for this work. Although the properties of the rods were similar, isotherms of the individual rods studied were all somewhat different. Water isotherms showed comparatively little hysteresis. The adsorption behavior of these rods differed considerably from the behavior of zinc chloride activated carbons with which we are familiar.

Helium

An especially pure commercial hydrogen-free helium was used (Air Reduction Sales Ltd., 99.99+% He). The helium was taken from a cylinder found satisfactory for use in a helium cryostat after passage through a liquid-

air-cooled charcoal trap. The helium was dried in our experiments by passage over solid KOH contained in a suitable high pressure vessel.

Nitrogen

Highest grade obtainable commercially (Dominion Oxygen Co., 99.7+%; < .03% O_2). The nitrogen was passed over KOH as in the case of helium.

2. Experimental Procedures and Methods

Water adsorption isotherms were determined by the McBain technique. Vessels containing the quartz spirals, manometers, etc. were all immersed in a large oil thermostatic bath maintained at about 25°C., but constant to within ±0.001°C. within short time intervals and probably to within ±0.1°C. during the eight month period of all of the experiments reported herein. Water vapor at controlled pressures was introduced into the adsorption apparatus by evaporation from a thoroughly outgassed water reservoir immersed in a second thermostatic bath.[10]

Nitrogen adsorption at high pressures was determined by expanding the gas at various pressures from a small high pressure capillary into a large volume attached to the vacuum system. The volumes were known and by comparison of the pressure relations between expansions with the carbon rod present and those with the rods absent, the "apparent" increase in volume of the capillary due to the presence of adsorbing carbon could be calculated for the various pressures. (Estimated error at higher pressures 5%, lower pressures 10%). At low pressures (down to 3×10^{-3} mm. Hg) expansions were made into a small capillary containing the active carbon on a different vacuum system. (Estimated error at pressures below 0.1 mm. Hg, about 20%.) In the case of helium similar measurements were made but the experimental errors were too large to give even qualitatively reliable adsorption data. The carbon rod helium density of 2.00 quoted above is that obtained at pressures of about half an atmosphere and not being corrected for helium adsorption is perhaps 5–10% too low.

Length Changes

The carbon rod was placed in a horizontal, heavy walled, large bore, pyrex capillary which was connected through a short length of high pressure steel tubing to a three way high pressure steel valve. The capillary could be opened to the high vacuum system and also to either a hydraulic high pressure oil pump and mercury separator, or to a cylinder containing gases at fairly high pressures.

The capillary containing the carbon rod (the ends of the rod were filed flat) was itself contained within a glass tube through which oil from the thermostat was circulated.

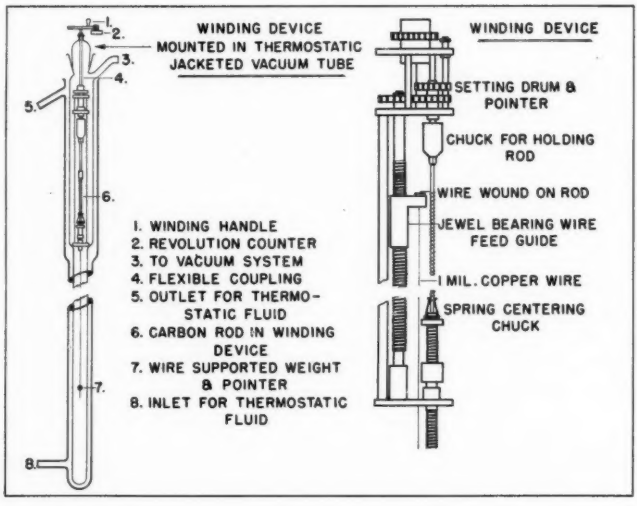
Length changes were observed by means of a travelling microscope. Reproducibility of individual length measurements was usually within $\pm 2 \times 10^{-3}$

[10] *The isotherm as plotted in Fig. 7 is based on the carbon weight obtained after a four day evacuation period following the water vapor equilibrations. This weight was less than the initial evacuated weight. The loss in weight is considered to be due to loss of chemisorbed or other material. The values of x/m used in the calculations were reduced by 0.014.*

mm. while reproducibility of length changes for various pressures was perhaps within 5×10^{-3} mm. Reproducibility of length measurements of the rod in vacuum on dismantling and reassembling the apparatus was $\pm 3 \times 10^{-2}$ mm.

It is considered that larger values of $\delta l/l$ are within $\pm$ 5%; small values, for example maximum contraction, within $\pm$ 20%.

Radial extensions were measured by means of a small winding device with which it was possible to observe the change in height of a small weight which was raised by winding a fine supporting wire on the carbon rod. Reproducibility in linear lift per 100 turns was usually within the reproducibility of the cathetometer, i.e., $\pm$ 0.05 mm., the total lift being of the order of 600 mm. The winding device was contained within a long vacuum tight glass tube which was surrounded with circulating thermostatic oil pumped from the large thermostat (25°C.). It may be remarked that considerable trouble was encountered owing to breakage of the bare one mil copper wire. The wire was tested for elastic deformation, elastic fatigue, etc., by making trial runs of 200 "winds" of 100 turns each in a number of ways which were more apt to cause breakage (e.g. larger weight, pulling wire over iron and glass rods, etc.). However, the trials were not made in vacuum. It was found that protection of the wire and winding apparatus from Hg vapor by means of a trap containing indium metal (liquid air cooled on evacuation) considerably prolonged the life of the wire. However, as a result of the frequent breakage of the wire, values of $\delta l/l$ corresponding to various changes in water vapor pressures as given in Fig. 9 do not represent a continuous series of extensions with a given setting. Considerable care was taken in the examination of the minimum and it is considered that it is real, the very small contraction being reliable perhaps within $\pm$ 50%. The extension at saturation is thought to be reliable within $\pm$ 20%. The winding apparatus is shown diagrammatically in the following sketch.



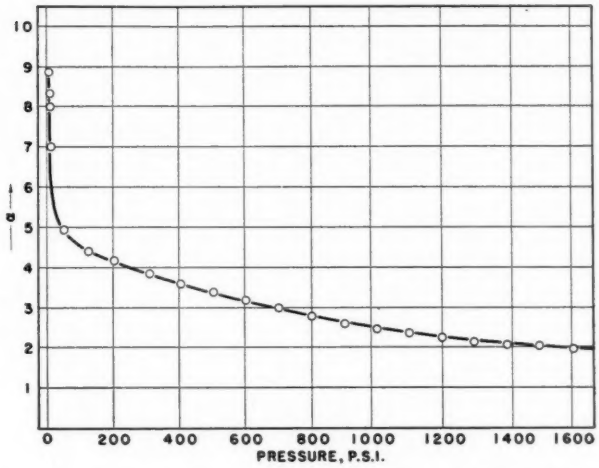


FIG. 6. Adsorption isotherm: Nitrogen on carbon rod No. 1 (25°C.). Ordinate, $a = \rho_a/\rho_g = \frac{\text{apparent void volume}}{\text{void volume}}$. Abscissa, nitrogen pressure.

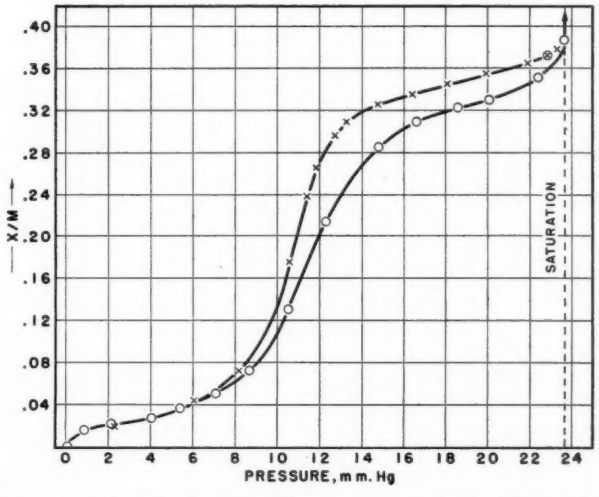


FIG. 7. Adsorption–desorption isotherm: Water vapor on carbon rod No. 1 (25°C.). Ordinate, weight of water adsorbed per gram carbon. Abscissa, water vapor pressure. (Cf. footnote 10)

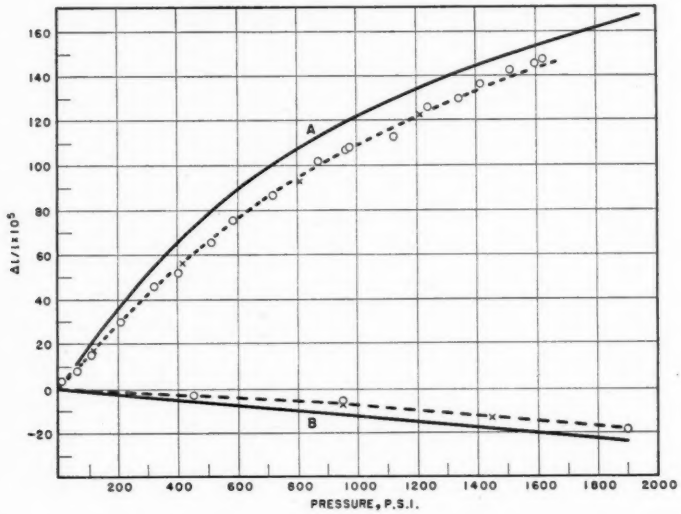


FIG. 8. Adsorption extension: Carbon rod No. 1 (25°C.); A, nitrogen; B, liquid water. Broken line drawn through experimental points; ○, adsorption; ×, desorption. Solid line calculated from: $\delta l/l = \frac{1}{3}\beta(1 + \phi K - \phi K\alpha)p_1$, $\beta = 3.3 \cdot 10^{-7}$/p.s.i.; $K = 2.91$; $\phi = 1.65$.

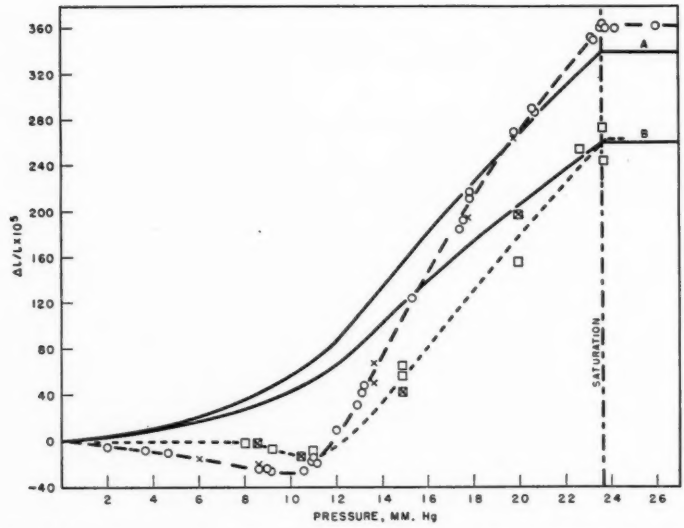


FIG. 9. Adsorption extension: Water vapor on carbon rod No. 1 (25°C.); A, axial extensions; B, radial. Broken line drawn through experimental points. Solid line calculated, Axial A, as for Fig. 8. Radial B, as for Fig. 8, but $K = 2.23$.

APPENDIX II—MODEL PORE SYSTEMS

The influence of pore shapes on the extensions of solids for given values of the changes of volumetric mean pressures, i.e., the relation of linear average pressures to volumetric average pressures, is, perhaps, best illustrated by reference to particular models.

Consider a thin section of a porous solid. Let the section have a thickness l_i and an area A_i consisting of the sum of the areas a_i and c_i. The area a_i represents the area of holes filled with fluid while the area c_i represents solid material. Let F_i be the total force acting normally on the area A_i so that the corresponding pressure $P_i = F_i/A_i$. Let F_{a_i} and F_{c_i} be the forces acting on the areas a_i and c_i respectively, the corresponding pressures being $p_{a_i} = F_{a_i}/a_i$ and $p_{c_i} = F_{c_i}/c_i$. Then we have $F_i = F_{a_i} + F_{c_i}$, and $A_iP_i = a_ip_{a_i} + c_ip_{c_i}$, and summing over all the sections,

$$\sum l_iA_iP_i = \sum l_ia_ip_{a_i} + \sum l_ic_ip_{a_i},$$

hence,

$$vP = v_ap_a + v_cp_c,$$

where $\sum l_iA_i = \sum v_i = v$ and $\sum v_iP_i = vP$ and p_a and p_c are similarly defined volumetric averages.

Let us now assume that the fluid-filled areas (i.e., the holes in the porous solid) are of two distinctly different kinds: (1) a number of small holes where the influence of the attractive forces is relatively large and where the pressures of the fluid differ from the hydrostatic pressure of the whole system, and (2) a smaller number of large holes where the effect of the attractive forces is small and the pressures are the same as that of the hydrostatic envelope. Thus we write

$$A_i = a_{1i} + a_{2i} + c_i$$

where A_i is subject to a net hydrostatic pressure P independent of l_i, while the area a_{1i} is subject to the pressure $P + p_{a_{1i}}$, the area a_{2i} to the pressure P, and the solid area c_i to the pressure $p_{c_i} = P + p_{c_i}'$. Then balancing forces in each section and summing over all of the sections l_i we get

$$P\sum l_iA_i = P\sum l_ia_{1i} + \sum l_ia_{1i}p_{a_{1i}} + P\sum l_ia_{2i} + P\sum l_ic_i + \sum l_ic_ip_{c_i}',$$

hence,

$$c_ip_{c_i}' = -a_{1i}p_{a_{1i}}$$

and

$$v_{a_1}p_{a_1} = v_a(p_a - P).$$

In order to introduce these relations into the compressibility formula

$$\delta l/l = -\tfrac{1}{3}\beta\sum l_ip_{c_i}/\sum l_i,$$

we must know a good deal about the actual structure of the material as well as something concerning the relations between fluid and solid stresses. If, for example, we assume that the hydrostatic pressure of the fluid within a micropore is uniform, so that the force per unit area within a given pore is the same in all directions, it implies that the corresponding equilibrium stresses in the walls of long thin capillaries are different in different directions. On the other hand, if we assume that the tensions in the solid surface are everywhere the

same, the hydrostatic pressure of the fluid in equilibrium with these tensions will differ in different directions. In the case of a comparatively very large capillary filled with liquid having concave menisci at its ends the bulk of the liquid will be under an almost uniform hydrostatic pressure, but the axial stress on the capillary wall will be considerably less than the radial stress. If, on the other hand, the change of the surface stress of the solid is assumed uniform, the corresponding change in axial and radial mean pressures of the fluid will not be the same. The former is a condition analogous to "capillary condensation" in large pores, the latter a condition describing adsorption in layers on a macroscopically uniform surface.

In addition to assumptions concerning the nature of the stresses, it is necessary to construct some sort of representative model pore system. For this purpose we assume that the porous body can be described as an assembly of rectangular or cubical cells of various sizes where the dimensions of the void space in each cell have constant relations to the cell dimensions. And we assume (*a*) that the fluid pressure $p_{a_{1i}}$ is constant everywhere within the void space of the cell, i.e., independent of l_i and independent of the cell dimensions, or we assume (*b*) that $c_i p_{c_i}' = \gamma\lambda_i$ where λ_i is the common perimeter of the areas a_{1i} and c_i, and where γ is the change in surface tension and is independent of l_i and independent of the cell dimensions. The latter assumption seems much more plausible generally as applied to active adsorbents, although as we have pointed out, for relatively large pores all of which were liquid filled and separated from vapor by menisci of constant curvature the former might be a fair approximation.

With these assumptions, we obtain for the two cases:

(*a*)
$$p_{c_i} = P - (a_{1i}p_{a_{1i}}/c_i),$$
$$\therefore \sum l_i p_{c_i}/\sum l_i = P - p_{a_1}[(\sum l_i a_{1i}/c_i)/\sum l_i]$$
$$= P - (v_a/v_{a_1})(p_a - P)[\sum l_i a_{1i}/c_i)/\sum l_i],$$

which with the compressibility relation leads to

[2*a*] $$\delta l/l = -\tfrac{1}{3}\beta(1 + \phi K_p - \phi K_p\alpha)\delta P$$

where $\delta p_a = \alpha\delta P$, $\phi = v_a/v_c$,

and $K_p = (v_c/v_{a_1})[(\sum l_i a_{1i}/c_i)/\sum l_i]$,

and α is defined by $p_a = \int_0^P \rho_a/\rho_1 \cdot dP = \alpha P$.

(*b*)
$$p_{c_i} = P + \gamma\lambda_i/c_i,$$
$$\therefore \sum l_i p_{c_i}/\sum l_i = P + \gamma[(\sum l_i\lambda_i/c_i)/\sum l_i$$

and
$$\gamma = -\sum l_i a_{1i}p_{a_{1i}}/\sum l_i\lambda_i = -v_a\, p_{a_1}/\sum l_i\lambda_i = -v_a(p_a - P)/\sum l_i\lambda_i,$$
$$\therefore \delta l/l = -\tfrac{1}{3}\beta(1 + \phi K_\gamma - \phi K_\gamma\alpha)P \qquad (2b)$$

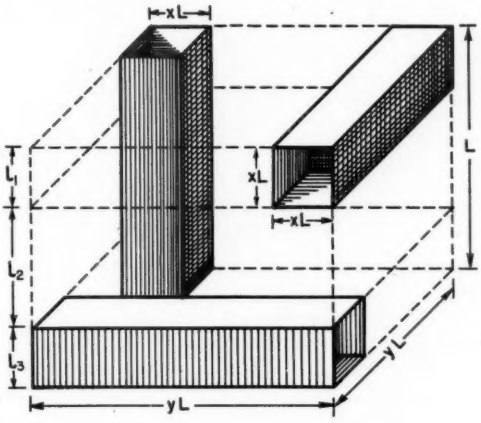
where
$$K_\gamma = v_c\cdot[(\sum l_i\lambda_i/c_i)/\sum l_i\lambda_i\cdot\sum l_i].$$

In both cases when c_i is constant, i.e., independent of l_i, $K_p = K_\gamma = 1$. Thus K_p and K_γ measure the ratios of the linear average pressures to the volumetric average pressures.

It will be noted that these formulae are dependent wholly on the relation of the micropore and solid structures and are independent of the macropore

structure. If we are interested in relating these extensions to extensions produced by the application of a force of tension to the whole system, as in measurements of Young's modulus, we must include both the macropore and the micropore structures in determining $\sum l_i p_{ci} / \sum l_i$. It is further to be noted that if we suppose that the porous body can be described as an assembly of rectangular or cubical cells of various sizes where the void space in each cell has a constant shape, the extensions are independent of the distribution of cell sizes but dependent only on the elastic behavior of the individual cell. The "average shaped cells" are more or less arbitrary representations of structural irregularities. We shall suppose the cells orientated so that the faces of the cells are parallel to the principal planes of stress. It will be noted that whatever the state of stress of a body, there will always exist three mutually perpendicular planes for which the tangential stress-components are zero; the stresses acting normally on these principal planes of stress behave essentially as pressures.

To illustrate the influence of cell shape on numerical values of K_p and K_γ we will consider two rather different model cells. The first model will be representative of a system of nonintersecting straight capillaries running through the specimen as shown in the following figure.



The capillaries are assumed square in cross section and of area x^2L^2. The cell has the dimensions $yL \cdot yL \cdot L$ (providing for lack of isotropy). Taking the axial length as L, the dimensions as function of l_i are

$l_1 = Lx$ $\lambda_1 = L(4x + 2y)$ $a_1 = L^2(x^2 + xy)$ $c_1 = L^2(y^2 - x^2 - xy)$
$l_2 = L(1 - 2x)$ $\lambda_2 = L4x$ $a_2 = L^2x^2$ $c_2 = L^2(y^2 - x^2)$
$l_3 = Lx$ $\lambda_3 = L(4x + 2y)$ $a_3 = L^2(x^2 + xy)$ $c_3 = L^2(y^2 - x^2 - xy)$

The values of x and y are limited by the following: Volume of void space (micropore) $= L^3x^2(1 + 2y)$. Volume of solid plus volume of micropore, i.e., the cell volume, $= L^3y^2$. (The cell structure is representative of the structure of the material surrounding the macropore space.) Hence, in the case of our carbon rods, $x^2(1 + 2y)/y^2 = 0.445$. Assuming the most unsym-

metrical arrangement consistent with the model, i.e., taking $x = 0.5$, then $y = 1.5$, and

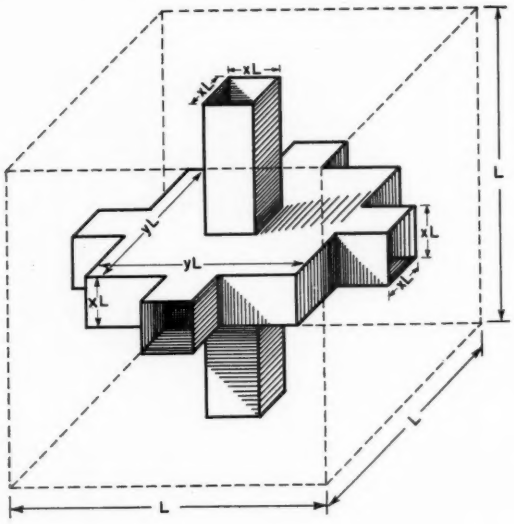
$$\phi K_p(\text{axial}) = 1.65,\ K_p = 1,$$
$$\phi K_\gamma(\text{axial}) = 1.65,\ K_\gamma = 1.$$

The corresponding expressions for radial extensions are:

$$\phi K_p = 2.20,\ K_p = 1.33,$$
$$\phi K_\gamma = 2.03,\ K_\gamma = 1.23.$$

The values for capillaries of circular cross section are essentially similar.[11]

X-ray diffraction studies indicate that the micropore system of activated carbon is a box-like structure formed from imperfect graphite-like platelets (6), the micropore void space constituting about one half of the void structure. The tensile strength of impervious graphite (Karbate) as given in the handbooks is about 2500 p.s.i. while the tensile strength of our samples is of the order of 400 p.s.i. The macropore system of many active carbons are fairly regular interstitial structures (our rods before activation have a tensile strength of $\sim$ 1000 p.s.i.). Thus it would appear that there should be areas along the axis where the micropore void space is about 80% of the micropore-solid system. The following model is representative of such a system.



For the model, taking $x = 0.395$ and $y = 0.90$, we get,

$$A \text{ axis, } \phi K_\lambda = 9.34,\ K_\gamma = 5.66,$$
$$B \text{ axis, } \phi K_\lambda = 1.42,\ K_\gamma = 0.860.$$

We may suppose the structure made up of filaments of cells of this type, a

[11]*It may be remarked that in the case of a cubical cell ($y = 1$), the elongation, due to a single capillary (square cross section x^2L^2) parallel to the axes of elongation, varies from 1/2 to 1/3 of that due to two similar capillaries whose axes are perpendicular to the elongation, i.e., K_p in the former case is $1/2(1 + x)$ times the value of K_p in the latter case.*

fraction of them arranged so that the A axes of the cells are parallel to the filament axes and the remainder of the cells arranged so that the B axes of the cells are parallel to the axes of the filament. Taking the fraction, 0.427, arranged so that the A axis of the cell is parallel to the axes of the filaments, we get

$$K_\gamma \text{ (axial)} = 2.91,$$
$$K_\gamma \text{ (radial)} = 2.23.$$

The plots of calculated extensions shown in Figs. 8 and 9 are based on these values of K_γ.[12] Thus the model micropore system is reasonably consistent with the strength of the material, its elastic properties and, in addition, consists of a box-like structure such as might be formed from graphite platelets. Of course, a great many alternative models can be devised that will describe the behavior of the rods, but these models are not by any means entirely arbitrary.[13]

It must be pointed out that if the shape of the average pore is not statistically independent of the surface free energy of the solid enclosing the average micropore, then K will become a function of p_1 and will probably vary with the nature of the adsorbable gas. Further, since the compressibility is not a true constant, but is unsymmetrical with respect to large compressions and expansions, Equation 16 must be regarded as an approximate representation of a more general formula which we may represent empirically as follows:

$$\delta l/l = -\tfrac{1}{3}\beta\bar{\delta}p_c \cdot e^{-h\bar{\delta}p_c}$$

and

$$\bar{\delta}p_c = \{1 + \phi K[1 + f(p)] - \phi K[1 + f(p)]\alpha\}\delta p_1.$$

While we might expect that in most cases $f(p)$ will be practically zero, the lack of constancy of the compressibility will not be negligible in cases where adsorption is large and the corresponding changes in states of stress of the solid are large. In the case of graphite the compressibility at 5000 p.s.i. is about 2% less than its compressibility at zero pressure (5). If activated carbon can be regarded as consisting essentially of graphite under stress, the stresses being largely removed when the rods are immersed in liquid water, the pure active carbon must be regarded as graphite under a compressive stress intensity of more than 5000 p.s.i., this large stress practically vanishing on immersion in liquid water.

It is important to note that the frequency distribution of cell sizes does not influence the values of $\delta l/l$ appreciably. This is in marked contrast to the influence of the frequency distribution of cell sizes on surface areas and permeabilities. These latter properties are dominated by the frequency distribution of cell sizes. While the elastic properties are almost wholly dependent

[12] ϕ = *total void volume/volume of carbon = 1.65 for this particular carbon.* ϕ *is independent of the model.*

[13] *It will be noted that the above treatment of the distribution of stress in the particular models assumes that stress contours in each section can be treated independently. This assumption ignores shearing and other distortional stresses and is, of course, a crude approximation. However, in the case of fine-grained isotropic porous material where deformations are very small, the mean stresses obtained by the above method will differ very little from those obtained by the much more laborious but more rigorous methods of the classical theories of elasticity.*

on the shape of the average micropore, the surface areas and permeabilities are almost entirely dependent on the ratios of the various statistical moments of the pore diameters, i.e., on the relative values of the mean pore diameter, the mean square, the mean cube, and the mean fourth power of the pore diameters. Thus adsorption–extension measurements can provide information concerning micropore structure that cannot be obtained directly from almost any other simple measurement, nearly all of the more readily measurable properties of active adsorbents being strongly dependent on frequency distributions of pore diameters. Adsorption–extension measurements and measurements of micropore permeability combined with B.E.T. surface area measurements and the results of X-ray diffraction studies should provide sufficient information from which to construct model micropore systems that are reasonably reliable representations of the real structure of some of these complex systems.

ACKNOWLEDGMENT

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THE SPECTRA OF SATURATED AND α–β UNSATURATED SIX-MEMBERED LACTAMS[1]

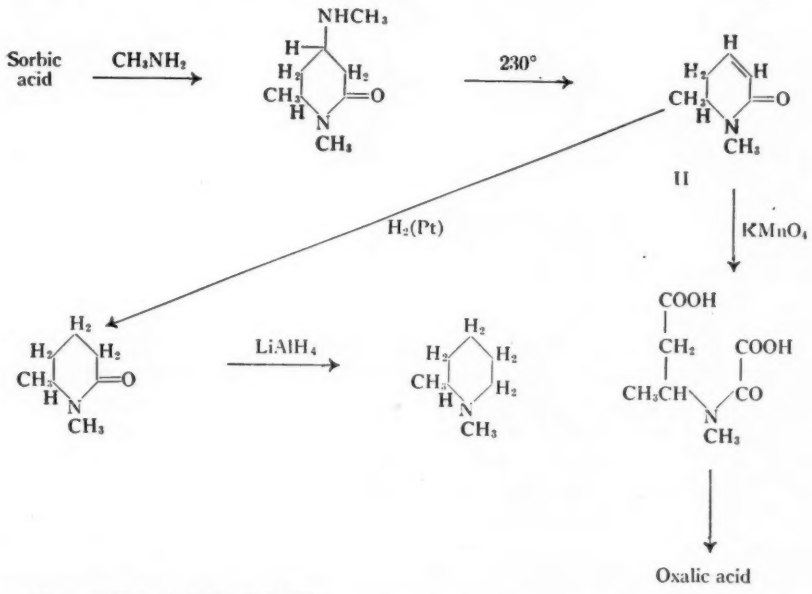
By O. E. Edwards and Tara Singh[2]

ABSTRACT

The ultraviolet and infrared spectra of some saturated and unsaturated six-membered lactams are described, and the unusual features in the 3μ and 6μ regions discussed. A comparison is made of these spectra with those previously ascribed to α–β unsaturated lactams.

On the basis of ultraviolet and infrared spectra, α–β unsaturated lactam structures have been assigned to products of Beckmann rearrangement of unsaturated oximes (8, 14) and to the alkaloid bakankosine (1). In addition an α–β unsaturated lactam structure has been considered for one of the transformation products of lycoctonine (5). It thus became of interest to examine the spectra of authentic α–β unsaturated lactams for comparison with those of the above compounds.

6-Methyl-5,6-dihydro-2-pyridone (I) and 1,6-dimethyl-5,6-dihydro-2-pyridone (II) were prepared by a method similar to that of Fischer and Schlotterbeck (7). The preparation and characterization of the latter is outlined below.



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[2]*National Research Council Postdoctorate Fellow.*

Since hydrolysis of the oxidation product from the unsaturated lactam gave oxalic acid in 75% yield, the lactam contained at least this percentage of the α–β unsaturated isomer.[3]

The 1,2-dimethyl piperidine gave a picrate analyzing correctly, and melting at 242° (the literature gives 241° (12)).

The ultraviolet spectra of the various compounds which have been assigned α–β unsaturated lactam structures are recorded in Table I. Our observations with 6-methyl-5,6-dihydro-2-pyridone contrast with the broad band (236–251 mμ) or series of maxima recorded by Linstead and co-workers (6). The positions of the maxima of all the compounds are similar, occurring at much longer wave lengths than for acyclic α–β unsaturated amides (2). As an example of the latter we have examined N-crotonylpiperidine,[4] and find it to have only a shoulder around 235 mμ.

The intensity of the maxima of the two six-membered α–β unsaturated lactams is considerably lower than those recorded for the seven-membered analogues and the bakankosine derivatives. Indeed, the spectra of the compounds related to bakankosine are more like those of α–β unsaturated ketones except that no long wave length (300–330 mμ) maxima are recorded.

The "iso" compounds derived from the periodate cleavage products of lycoctonine (5) have λ_{max} 219 mμ, 20 mμ lower than the simple α–β unsaturated lactams which have been studied. This raises doubt as to the unsaturated lactam postulate.

The origin of the bands in the 3μ and 6μ regions in the infrared spectra of amides has been the subject of considerable controversy (9, 15, 16). The

TABLE I
ULTRAVIOLET SPECTRA IN ETHANOL

Compound	λ_{max} in mμ	ϵ_{max}	Reference
Bakankosine derivatives	236–242	12,000–18,000	1
3,5,5-Trimethyl-7-amino-2-heptenoic acid lactam	237	7,320	14
3,5-Dimethyl-7-amino-2-heptenoic acid lactam	241	—	8
6-Methyl-5,6-dihydro-2-pyridone	241	1,470	
1,6-Dimethyl-5,6-dihydro-2-pyridone	251	1,120	

strong band in the 6μ region observed with aliphatic amides has been associated with the C=O stretching vibration (9,13,15). Saturated N-alkyl six-membered lactams have a strong band near 1640 cm.$^{-1}$ when in carbon disulphide solution or in the liquid or solid state (mull). This band is displaced to near 1625 cm.$^{-1}$ in chloroform solution (Table II). The peak is often asymmetric but in the simple compounds so far examined no second band has been clearly resolved. In contrast to these the spectrum of N-crotonylpiperidine has two bands, and the spectra of the two α–β unsaturated lactams have three bands

[3]*The equilibrium between acyclic α–β and β–γ unsaturated acids and esters at moderate temperatures lies over 65% on the α–β side (11). The position of the equilibrium in the above dihydropyridone seems the same at 230° as at room temperature, since no change in ϵ_{max} was observed when I was left at room temperature in 1 N alkali for six hours.*

[4]*The authors are indebted to Dr. F. A. L. Anet for a sample of this amide.*

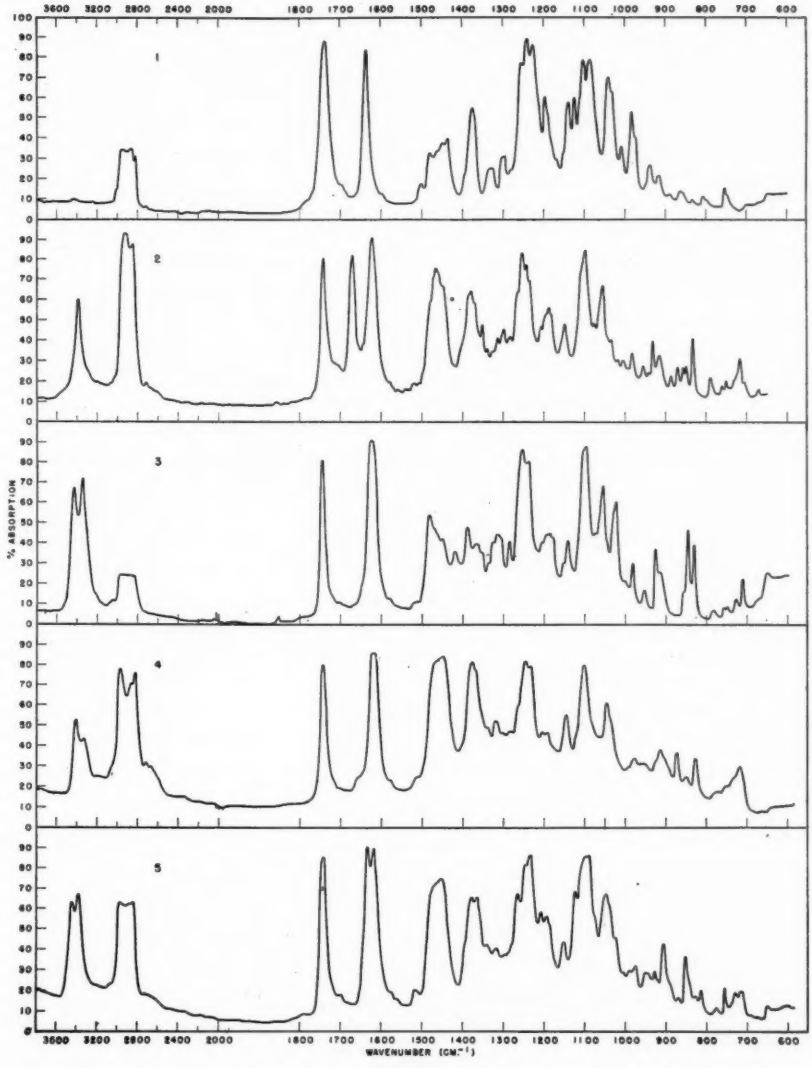

FIG. 1. Infrared spectra of: 1. 6-methyl-5,6-dihydro-2-pyridone (chloroform), 2. 1,6-dimethyl-5,6-dihydro-2-pyridone (liquid), 3. 1,6-dimethyl-5,6-dihydro-2-pyridone (chloroform), 4. N-crotonylpiperidine (liquid), 5. 1,6-dimethyl-2-piperidone (liquid). The background trace in 1 and 3 is that obtained when both cells were filled with pure chloroform.

in the 1600–1700 cm.$^{-1}$ region (Fig. 1). No bands occur in the 1500–1600 cm.$^{-1}$ region in the saturated or unsaturated lactams.

The C=C and C=O stretching bands in the α–β unsaturated amides would be expected to lie in the 1610–1630 cm.$^{-1}$ region since conjugation usually shifts

both toward smaller wave numbers. The C=C band should as usual be very much weaker than the C=O band. The CN band according to Letaw and Gropp (10) should lie between 1600 and 1650 cm.$^{-1}$. A possible explanation of the spectra actually found is that the three vibrations have very close to the same fundamental frequency, and that resonance between them results in split bands of higher and lower frequency with very much modified relative intensity.

The "iso" compounds derived from lycoctonine have single bands near 1650 cm.$^{-1}$ which lends no support to the unsaturated lactam suggestion.

The infrared spectra of bakankosine derivatives resemble that of N-crotonylpiperidine more than that of 6-methyl-5,6-dihydro-2-pyridone (the 1610 cm.$^{-1}$ band is more intense than the 1670 cm.$^{-1}$ band). However, the alkaloid spectra could as readily be interpreted as that of α–β unsaturated ketones (1670 cm.$^{-1}$) with an isolated hydrogen bonded lactam (1610 cm.$^{-1}$). (See the discussion of ultraviolet spectra.)

The hydrogen on the double bonds (*cis* disubstituted in I and II) shows up in the infrared near 3040 cm.$^{-1}$ (CH stretching) and probably (3) in the strong band at 805–820 cm.$^{-1}$ (CH bending). It is interesting that the 3040 band does not appear in the spectrum of the N-alkyl lactam II taken in chloroform.

The band at 2800 cm.$^{-1}$ in 4-methylamino-1,6-dimethyl-2-piperidone can most probably be assigned to the C–H stretching of the methyl group on the basic nitrogen since the N-methyl lactams do not show it.

The 3400–3500 cm.$^{-1}$ bands in the spectra of liquid films of N-dialkyl amides have been noted by Letaw and Gropp (10). They consider them to be overtones of the 1600–1700 cm.$^{-1}$ bands. We have observed with lupanine (4) and in the present work that this band does not appear in the spectra in chloroform or carbon disulphide solutions. It is much too intense for an overtone, and in addition, it is at too high a wave number (first overtones usually appear at a wave number very close to double the parent wave number). Thus the only simple explanation of this band appears to be that in the liquid state N-alkyl lactams exist to a considerable extent as the enol. Although lupanine gave no methane in the Zerewitinoff determination, freshly distilled II and 1,6-dimethyl-2-piperidone gave close to one mole at 100°, indicating the mobility of the hydrogens α (or γ) to the carbonyls.

The two lactams with an NH (I and 2-piperidone) in chloroform solution had sharp bands near 3400 cm.$^{-1}$ (free NH) and broader bands of similar intensity near 3200 cm.$^{-1}$ (bonded NH). In the spectra of the pure substances, however, the 3400 cm.$^{-1}$ band was absent but the 3200 cm.$^{-1}$ one was much more intense.

A study of saturated N-alkyl lactams in which enolization is blocked by alkyl substitution, or which contain N^{15}, and α–β unsaturated N-alkyl lactams with the double bond carbons substituted might clarify the origin of the infrared spectra in the 3 and 6μ regions.

A summary of the position of the bands in the 1600–1700 cm.$^{-1}$ region of some saturated and α–β unsaturated six-membered lactams is given in Table II.

TABLE II

Lactam	Position of band, cm.$^{-1}$	State[a]
Saturated —CONHR		
2-Piperidone[b]	1670	Liquid film
	1665	Chloroform solution
Saturated —CONHR$_2$		
3-Carbethoxy-4-quinolizidone[b]	1643	Liquid film
	1631	Chloroform solution
Lupanine[c]	1642	Liquid film
	1624	Chloroform solution
Oxysparteine[c]	1640	Carbon disulphide solution
4-Methylamino-1,6-dimethyl-2-piperidone	1637	Liquid film
1,6-Dimethyl-2-piperidone	1637	Liquid film
α-β Unsaturated —CONHR		
6-Methyl-5,6-dihydro-2-pyridone	1610, 1677	Nujol mull
	1615, 1675	$CHCl_3$ solution
α-β Unsaturated —CONHR$_2$		
1,6-Dimethyl-5,6-dihydro-2-pyridone	1611, 1643, 1667	Liquid film
	1609, 1634, 1664	Chloroform solution

[a] *The concentration of the chloroform solutions was approximately 30 mgm. per ml.*
[b] *The authors gratefully acknowledge the gift of samples from Dr. L. Marion and Dr. H. J. Vipond.*
[c] *See Reference (4).*

EXPERIMENTAL

The ultraviolet spectra were taken on a Beckmann model D.U. spectrophotometer using 95% ethanol as solvent. The infrared spectra were determined on a Perkin-Elmer model 21 double-beam spectrophotometer with a sodium chloride prism. Percentage absorption is indicated in brackets after the wave number in cm^{-1}.

4-Methylamino-1,6-dimethyl-2-piperidone

Twelve grams of methylamine was condensed into a pressure tube containing 2 cc. of water and 4.0 gm. of sorbic acid. The tube was sealed and heated at 150° for 60 hr. The contents of the tube were transferred to a distilling flask and the methylamine boiled off, finally under reduced pressure. Preliminary experiments showed that only a trace of free acid was left after the 60 hr. treatment. The residual liquid was distilled and a fraction was collected at 93–94° under 0.3 mm. pressure (4.5 gm., 80%). Found: N, 17.56. Calc. for $C_8H_{16}ON_2$: N, 17.95. Infrared spectrum (liquid film): 3460 (40), 3300 (46), 2950 (56), 2800 (39), 1637 (87), 1490 (60), 1475 (58), 1458 (60), 1425 (46), 1402 (61), 1377 (55), 1330 (63), 1286 (36), 1260 (34), 1241 (42), 1170 (29), 1135 (44), 1120 (40, shoulder), 1084 (33, shoulder), 1060 (31), 1032 (25), 973 (19). The spectrum in the fingerprint region was not sharp. The amino lactam did not readily give a crystalline hydrochloride or perchlorate. It formed a crystalline picrate when picric acid in benzene was added to a benzene solution of the base. This was recrystallized from 50% ethanol–water from which it separated as long stout prisms, m.p. 187–189°. Found: C, 43.77; H, 4.78. Calc. for $C_{14}H_{19}O_8N_5$: C, 43.64; H, 4.97.

1,6-Dimethyl-5,6-dihydro-2-pyridone

When 4-methylamino-1,6-dimethyl-2-piperidone was refluxed with a solution of 3 gm. of barium hydroxide octahydrate in 20 cc. of water, methylamine was slowly evolved. However, after eight hours the bulk of the amine was recovered unchanged.

At 150° the amino lactam evolved methylamine but the conversion was very slow.

The amino lactam (17.0 gm.) was decomposed by refluxing for seven hours in a nitrogen atmosphere and then slowly distilling the product at one atmosphere. The weight loss on the refluxing was 3.0 gm. (theory for 1 mole of methylamine 3.38 gm.). The distillate was dissolved in 10 cc. of 50% sulphuric acid. Fifty grams of sodium sulphate was added, the solid broken up, and then thoroughly extracted with methylene chloride. The solvent yielded 13.0 gm. of neutral oil. This was distilled at 155–157° under 130 mm. pressure, giving 10 gm. (73%) of colorless oil with a pleasant odor. Five grams of the oil was fractionated at one atmospheric pressure giving

Cut 1, b.p. up to 225°, n_D^{26}1.4952;
Cut 2, b.p. 225–228°, n_D^{26}1.4953;
Cut 3, b.p. 228–230°, n_D^{26}1.4960.

Cut 2 had λ_{max} 251 mμ, log ε 3.05, and cut 3 had λ_{max} 251 mμ, log ε 3.12. Cut 2 was analyzed. Found: C, 66.69; H, 8.98; active hydrogen, 0.627, 0.646. Calc. for $C_7H_{11}ON$: C, 67.17; H, 8.86; one active hydrogen, 0.805. Infrared spectra (see Fig. 1). Liquid film: 3480 (24), 3040 (14), 2980 (38), 2940 (35), 1667 (84), 1643 (81), 1610 (74), 1483 (51), 1450 (50), 1403 (60), 1377 (38), 1326 (51), 1294 (24), 1250 (40), 1162 (17), 1111 (41), 1073 (18), 1038 (35), 990 (18), 931 (10), 883 (7), 853 (16), 821 (45), 788 (26), 758 (9), 715 (34), 682 (19), 692 (22). Chloroform solution, 1 mm. cell: 3660 (10), 2980 (59), 2460 (10), 1755 (12), 1666 (94), 1631 (92), 1608 (92). Cut 1 (400 mgm.) was dissolved in 1 cc. of 0.1 *N* sodium hydroxide and allowed to stand at 25° for six hours. The solution was made just acid, six grams of sodium sulphate added, and the lactam extracted with methylene chloride. The resulting oil was distilled at a bath temperature of 65–70° under 0.2 to 0.3 mm. pressure. The distillate had λ_{max} 251 mμ, log ε 3.05.

The unsaturated lactam (625 mgm.) was oxidized at 0° in aqueous solution with 2.1 gm. of potassium permanganate. After filtration and acidification the solution was extracted continuously with ether. The 1.1 gm. of thick oily acid which was extracted could not be induced to crystallize. A sample of this oil (150 mgm.) was refluxed with 4 cc. of 10% sodium hydroxide solution for six hours. The solution was cooled, acidified with hydrochloric acid, and filtered from a trace of white precipitate. A solution of 0.5 gm. of calcium chloride in 1 cc. of water was added, and the mixture made alkaline to litmus with aqueous ammonia. The white gelatinous precipitate was coagulated by boiling and collected by centrifuging. After washing by suspension in water and centrifuging again, the precipitate was dried to constant weight. Yield: 75.6 mgm. (75% of theory for calcium oxalate). The salt from hydrolysis

of 450 mgm. of oily acid was decomposed with 2 cc. of 6 *N* hydrochloric acid and the organic acid extracted into ether. The ether on evaporation left a crystalline mush. This was recrystallized from hot water after which it melted at 95–100°, resolidified, and melted at 189° (dec.). A mixture of this with oxalic acid hydrate behaved in an identical manner.

1,6-Dimethyl-2-piperidone

A solution of 130 mgm. of 1,6-dimethyl-5,6-dihydro-2-piperidone in 10 cc. of ethanol in the presence of platinum from 30 mgm. of platinum oxide (Adams') absorbed 26.1 cc. of hydrogen at 21°C. and 760 mm. pressure in 15 min. The rate of hydrogen uptake then fell off very markedly. The solution was filtered and concentrated below room temperature under reduced pressure. The residual liquid was distilled at a bath temperature of 80–85° under 1 mm. pressure. The distillate had n_D^{24}1.4802. Found: C, 66.04; H, 10.18; active hydrogen, 0.487. Calc. for $C_7H_{13}ON_2$: C, 66.10; H, 10.30; one active hydrogen, 0.792. Infrared spectrum (liquid film, Fig. 1): 3460 (52), 2950 (70), 1637 (87), 1490 (65), 1475 (64), 1451 (63), 1422 (55), 1402 (71), 1382 (57), 1337 (73), 1311 (46), 1250 (57), 1186 (52), 1140 (40), 1101 (30), 1056 (60), 1026 (35), 1000 (21), 909 (22), 850 (20), 688 (32), 657 (38), 645 (39).

1,2-Dimethylpiperidine (N-Methyl pipecoline)

The above 1,6-dimethyl-2-piperidone (300 mgm.) was dissolved in 15 cc. of anhydrous ether and 1 gm. of lithium aluminum hydride added. Fifteen cubic centimeters of dioxane was added, and the ether boiled off. The dioxane solution was then refluxed for 30 min. The excess hydride was decomposed by slow addition of methanol, following which the dioxane, methanol, and amine were distilled together under reduced pressure (boiling point around 70°). Twenty cubic centimeters of dioxane was added to the residue and this distilled. To the combined distillate was added 500 mgm. of picric acid. When this solution was concentrated to 10 cc., 600 mgm. of picrate crystallized. The picrate crystallized from ethanol as yellow feathery crystals, m.p. 242° (literature m.p. 240–241°). Found: C, 45.76; H, 5.34. Calc. for $C_{13}H_{18}N_4O_7$: C, 45.61; H, 5.30.

6-Methyl-5,6-dihydro-2-pyridone

This was prepared as described by Fischer and Schlotterbeck (7). When recrystallized from ethyl acetate – petroleum ether it separated as needles, m.p. 105–106°. Found: C, 65.02; H, 7.98. Calc. for C_6H_9ON: C, 64.84; H, 8.16. Ultraviolet spectrum: λ_{min} 235 mμ, log ε 3.15; λ_{max} 241 mμ, log ε 3.17. Infrared spectrum (nujol mull): 3180 (71), 3060 (54), 2930 (52), 1677 (90), 1660 (81, shoulder), 1610 (79), 1475 (41), 1447 (43), 1420 (67), 1381 (30), 1370 (33), 1355 (26), 1326 (77), 1300 (34), 1210 (19), 1199 (21), 1153 (42), 1100 (20), 1075 (19), 981 (11), 939 (22), 885 (34), 820 (57, shoulder), 812 (72), 757 (29), 697 (30), 655 (23). Chloroform solution (31 mgm. per ml., 0.1 mm. cell): 3400 (29), 3220 (27), 3000 (53), 2890 (27), 1675 (97), 1615 (80), 1442 (55), 1400 (28), 1385 (30), 1363 (33), 1345 (28), 1321 (51), 1300 (26), 1145 (46), 1100 (21), 878 (28), 807 (54).

N-Crotonylpiperidine

This boiled at 117–119° under 10 mm. pressure, and had n_D^{25}1.5090. Ultraviolet spectrum: log ϵ 4.04 (215 mμ); 3.82 (235 mμ). Infrared spectrum (liquid film) (see Fig. 1): 3500 (25), 3220 (12), 2940 (93), 2860 (87), 1664 (98), 1617 (99), 1449 (75), 1369 (60), 1353 (62), 1314 (37), 1285 (94), 1253 (92), 1220 (97), 1162 (25), 1140 (80), 1129 (59), 1103 (64), 1024 (78), 971 (90), 922 (54), 891 (34), 851 (68), 819 (42), 798 (29), 675 (39).

2-Piperidone

A sample of the lactam was purified by dissolving in 3 *N* sulphuric acid, salting out with anhydrous sodium sulphate, and extraction into methylene chloride. After distillation under 10 mm. pressure the compound crystallized readily. The hygroscopic solid melted at 38°. Infrared spectrum: (*a*) Thin liquid film: 3220 (45), 3090 (31), 2950 (53), 2880 (41), 1670 (89), 1500 (58), 1475 (36), 1452 (34), 1415 (44), 1356 (55), 1330 (49), 1310 (44), 1273 (23), 1182 (25), 1170 (35), 1115 (34), 1060 (17), 990 (17), 939 (28), 829 (31), 769 (30), 656 (33). (*b*) Chloroform solution (32.4 mgm. per ml., 0.1 mm. cell): 3400 (28), 3290 (18), 3220 (26), 3000 (57), 3970 (57), 2890 (34), 1665 (97), 1499 (59), 1474 (36), 1454 (32), 1416 (32), 1395 (32), 1356 (59), 1334 (47), 1309 (38), 1274 (30), 1182 (22), 1170 (40), 1106 (27), 1060 (18), 988 (18), 936 (21), 825 (17).

3-Carbethoxy-4-quinolizidone

A chloroform solution of the compound was washed with dilute acid and with sodium carbonate solution. The residual oil after removal of the chloroform was distilled under 0.2 mm. pressure (bath temperature, 130°). Found: C, 64.31; H, 8.81; N, 6.35. Calc. for $C_{11}H_{19}O_3N$: C, 63.97; H, 8.50; N, 6.22. Infrared spectrum (liquid film): 3450 (12, broad), 2940 (68), 2860 (49), 1736 (84), 1644 (90), 1470 (66), 1446 (71), 1392 (32), 1370 (56), 1351 (51), 1320 (55), 1300 (45), 1263 (69), 1219 (58), 1180 (75), 1120 (44),1100 (51), 1145 (43), 1135 (44), 985 (21), 975 (22), 916 (11), 897 (11), 850 (27).

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THE MECHANISM OF PERSULPHATE OXIDATIONS[1]

By R. L. Eager and K. J. McCallum

ABSTRACT

It has been found that exchange between persulphate and sulphate, in both concentrated acetic acid as solvent and in aqueous solution, is not more than one half of one per cent complete in 12 hr. at 34.2°C. This indicates that the equilibrium proposed by Levitt, $S_2O_8^= \rightleftarrows SO_4^= + SO_4$, probably plays no part in persulphate oxidations.

INTRODUCTION

It has been proposed by Eager and Winkler (1) that the first and rate controlling step in the reaction between potassium persulphate and mercaptans, using concentrated acetic acid as solvent, is

$$S_2O_8^= \rightleftarrows 2SO_4^{\bar{}}. \qquad [1]$$

Recently, Levitt (4) suggested, for both this solvent and aqueous systems, a new mechanism for persulphate oxidations in which the above reaction is replaced by the following:

$$S_2O_8^= \rightleftarrows SO_4^= + SO_4. \qquad [2]$$

According to either mechanism, the reactive intermediate, $SO_4^{\bar{}}$ or SO_4, may then react with mercaptan. For high mercaptan concentrations the rate at which persulphate disappears will be equal to that of the forward reaction of [1] or of [2]. Levitt applied his mechanism to the data of Eager and Winkler and found good agreement between the observed and calculated dependence of the specific rate constant on the initial mercaptan concentration. However, this same dependence is required by the mechanism of Eager and Winkler if the Franck–Rabinowitsch "cage effect" (2) is assumed to apply to Reaction 1.

Levitt points out that according to his proposed mechanism sulphate ions should retard the rate of reaction of persulphate. Actually, Eager and Winkler found that sulphate ions increased the rate constant, apparently through a salt effect. Moreover, in some cases at least, when retardation by sulphate ions occurs, it might be due to a mechanism other than that proposed by Levitt. Green and Masson (3) found, in their investigations on the decomposition of aqueous solutions of various persulphates and of persulphuric acid, that sulphate ions caused a retardation of the rate of decomposition which was attributable to a salt effect.

Apart from the above considerations there appears to be a simple way in which to determine whether Levitt's suggestion at least represents a possible mechanism. It is implicit in his mechanism that equilibrium must be established between $S_2O_8^=$ ions and $SO_4^=$ ions in times that are short compared with those used in the rate studies (1). Otherwise the predicted and the observed kinetics would not agree. This means that if sulphate ions labelled with radioactive sulphur are present in solution with inactive persulphate ions, there should be rapidly established a uniform distribution of radioactive sulphur between sulphate and persulphate ions.

[1]*Manuscript received February 2, 1954.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

Previous work in these laboratories (5) indicated that, in aqueous solution and at room temperature, no exchange of radioactivity occurred between sulphate ions labelled with radioactive sulphur and inactive persulphate ions over a period of a few hours. The present paper presents the results of a more detailed study of the exchange in both aqueous solution and in the concentrated acetic acid solvent used by Eager and Winkler.

EXPERIMENTAL AND RESULTS

Exchange Experiments

A solution of S^{35}-labelled sodium sulphate and inactive potassium persulphate was allowed to stand for a given length of time at 34.2°C.* An excess of barium chloride was then added and the precipitated barium sulphate removed by centrifugation. The remaining solution, containing the persulphate and excess barium chloride, was heated to 80–90°C. for approximately 12 hr. At these temperatures the persulphate slowly decomposes (3) to form sulphate, which also precipitates as barium sulphate. From the specific activities of the two barium sulphate precipitates the extent of the exchange could be calculated. As a check on the amount of radioactivity present, control experiments were made in which no potassium persulphate was added.

Two preliminary experiments, in which no undue care was taken in the separation involved, were made to determine approximately the extent of exchange between sulphate and persulphate. In one of these experiments the solvent was water while in the other experiment the solvent was the acetic acid – water mixture used by Eager and Winkler (1). If, as indicated by the previous work, the exchange was found to be small or negligible, then such factors as exchange during separations could be neglected in more carefully controlled experiments. The centrifugate from the acetic acid solution was cloudy with barium sulphate, while small crystals of barium sulphate were observed in the centrifugate from the aqueous solution. A second centrifugation failed to prevent some carry-over of barium sulphate in both experiments. It is likely that the carry-over of precipitate was due to the use of 50-ml. round-bottomed centrifuge tubes and to removal of the centrifugates by decantation.

The results are given in Table I. The extent of exchange in the concentrated acetic acid solvent, Experiment 1, is $2.2 \pm 0.3\%$, and in water, Experiment 2, it is $2.0 \pm 0.2\%$.

While these results indicated that the possibility of Reaction 2 occurring to any appreciable extent is very unlikely, it seemed desirable to repeat the experiments with more careful separation of the sulphate from the persulphate. Fifteen-milliliter centrifuge tubes with pointed ends were used, which permitted the centrifugates to be removed with a pipette without seriously disturbing the precipitates. The centrifugates appeared perfectly clear, but as an additional precaution they were scavenged with inactive barium sulphate. To each was added an inactive sodium sulphate solution and the scavenging precipitate of barium sulphate was centrifuged off and discarded.

**Most of the earlier rate studies were made at 35°C.*

TABLE I

EXCHANGE BETWEEN PERSULPHATE AND SULPHATE

Temperature, 34.2±0.1°C. Potassium persulphate concentration, 0.000766 gm. moles per liter. Sodium sulphate concentration, 0.00153 gm. moles per liter

Expt. No.	Time, hr.*	Solvent	Source of $BaSO_4$	Specific activity** of $BaSO_4$: counts/mgm.
1	12.1	Conc. acetic acid	$SO_4^=$ $S_2O_8^=$	128±1*** 1.4±0.2
2	13.0	Water	$SO_4^=$ $S_2O_8^=$	178±2 1.8±0.1
3	Control	Water	$SO_4^=$	166±2
4	12.4	Conc. acetic acid	$SO_4^=$ $S_2O_8^=$	141±1 0.45±0.13
5	12.4	Water	$SO_4^=$ $S_2O_8^=$	169±1 0.39±0.10
6	Control	Water	$SO_4^=$	192±1

The times for the aqueous and for the acetic acid media were taken from addition of labelled sulphate, or addition of acetic acid, respectively, until addition of barium chloride.

***Corrected for background and for thickness of sample.*

****Only the statistical errors of counting were considered when calculating the standard deviations.*

Since the preliminary experiments indicated a maximum exchange of only about 2% in 12 hr., the amount of back exchange from persulphate to sulphate during the short scavenging time would be negligible.

The results are also given in Table I. The extent of exchange in the concentrated acetic acid, Experiment 4, was 0.64 ± 0.19%, and in water, Experiment 5, it was 0.46 ± 0.12%.

DISCUSSION

The values found for the exchange between sulphate and persulphate may be the result of true exchange, of exchange induced by separation, of incomplete separation, or of some combination of these. In any event, the results do set, for the solvents used, an upper limit of approximately 0.5% for the extent of exchange between sulphate and persulphate in a 12 hr. period at 34.2°C.

As mentioned earlier, if Levitt's proposed mechanism is correct, the exchange between sulphate and persulphate should be essentially complete in times that are short compared with those used in the previous rate studies (1). From the data of Eager and Winkler it is estimated, for the potassium persulphate and sodium sulphate concentrations used in the present work, that the first order rate constant with respect to the persulphate concentration will be approximately 0.2 $hr.^{-1}$, if excess mercaptan were present. This means that two thirds of the persulphate would have reacted in a 5.5 hr. period. In many of the rate experiments the reactions were allowed to proceed to this extent. Since the value of 0.2 $hr.^{-1}$ for the value of the observed rate constant is that found when excess mercaptan is present, then on the basis of the proposed mechanisms this is also the value of the specific rate constant for the

decomposition of persulphate into the reactive intermediates. From this value for the specific rate constant, it may be calculated that each persulphate ion has *on the average* been in the reactive intermediate form 2.5 times in the 12.4 hr. period used in the present exchange studies. Alternatively, the time for the half-life of the forward reaction may be calculated and is found to be 3.7 hr. From this value for the half-life it follows that in a 12.4 hr. period, slightly more than 91% of the persulphate was in the reactive intermediate form *at least once*. From the observed stability of potassium persulphate in the solvents used the specific rate constant for the recombination of the intermediates must be very large. Hence there has been a good opportunity for close to 90% exchange to have occurred if Levitt's mechanism is operative. Since the exchange actually found was much less than 90% it would appear from the above considerations that the equilibrium proposed by Levitt is relatively unimportant in the reactions of persulphates in aqueous or in concentrated acetic acid solutions. It is still possible that SO_4 is an intermediate in persulphate oxidations, but if so, it must occur in some reaction other than a reversible one involving sulphate and persulphate ions.

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THE SYSTEM LITHIUM SULPHATE – AMMONIUM SULPHATE – WATER[1]

By A. N. Campbell, W. J. G. McCulloch, and E. M. Kartzmark

ABSTRACT

The binary eutectics $Li_2SO_4 \cdot H_2O$ – ice and $(NH_4)_2SO_4$ – ice as well as the ternary eutectics $Li_2SO_4 \cdot H_2O$ – $Li_2SO_4 \cdot (NH_4)_2SO_4$ – ice and $(NH_4)_2SO_4$–$Li_2SO_4 \cdot (NH_4)_2SO_4$–ice have been determined as to temperature and composition. The complete solubility isotherms at 0.1°, 71.8°, and 95.2°C. have been investigated. The enthalpies of solution of lithium sulphate monohydrate, of ammonium sulphate, and of double salt have been determined (in water at room temperature), and from these data, as well as from the solubility isotherms, it has been shown that the temperature of the transition of the double salt, $Li_2SO_4 \cdot (NH_4)_2SO_4$, to its component single salts (in the presence of water) is approached by lowering the temperature, but this transition temperature is still far from reached when the system freezes completely.

INTRODUCTION

A double salt of the formula $Li_2SO_4 \cdot (NH_4)_2SO_4$ was known to form in the above system but no transition point had been established for the reaction:

$$Li_2SO_4 \cdot H_2O + (NH_4)_2SO_4 \rightarrow Li_2SO_4 \cdot (NH_4)_2SO_4 + H_2O.$$

In the corresponding system $Na_2SO_4 - (NH_4)_2SO_4 - H_2O$, the transition temperature is well known to be 59.3° (11, 4, 5), the double salt being unstable above this temperature; there is also a lower transition temperature at −16°C., but the situation is complicated by the fact that sodium sulphate is anhydrous at the higher transition temperature but hydrated, as Glauber's salt, at the lower. We therefore decided to investigate several isotherms of the above system, as well as the ternary eutectics, with a view to predicting the transition temperature, by extrapolation in the usual manner.

The component binary systems ammonium sulphate – water and lithium sulphate – water* are well known, but there has been some controversy about the lithium sulphate – water system. In a previous paper, one of us (3) determined the complete equilibrium diagram of the system, with the exception of the critical data for water in the presence of lithium sulphate. Some of these data were again checked in the present work. The most debatable point is the composition of the eutectic ice – $Li_2SO_4 \cdot H_2O$, which Campbell was only able to obtain by extrapolation. Another point at issue was the claim of Friend (6) that at low temperatures a dihydrate of lithium sulphate exists, a claim which Campbell was unable to verify.

The double salt of ammonium and lithium sulphates is congruently soluble and is therefore readily prepared by dissolving stoichiometric quantities of the constituent salts in water and crystallizing out. Schreinemakers (17) has determined the solubility of the pure double salt in water at temperatures ranging from −10°C. to 70.0°C., and he found the solubility to be nearly

[1]*Manuscript received March 30, 1954.*
Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Man.
**The binary lithium sulphate – ammonium sulphate has only a theoretical existence, at least over the greater part of the curve, since lithium sulphate melts some seven hundred degrees above the temperature at which ammonium sulphate decomposes.*

independent of temperature. Schreinemakers' results, however, cannot be quite correct, since they show an increase of solubility from 35.25% at −10°C. to 36.18% at 70°C., but our calorimetric work, described in this paper, shows that the enthalpy of solution, though small in saturated solution, is definitely negative and this, of course, is incompatible with a solubility increasing with temperature. Schreinemakers has also determined the ice-line in the pseudobinary system water – double salt, and from the intersection of this curve with the solubility curve he has determined the pseudobinary eutectic ice – double salt, to contain 35.15% double salt and to lie at a temperature of −20.7°C., a temperature which he verified by direct experiment.

Schreinemakers and Cocheret (17) have determined the complete isotherms of the ternary system at 30°C. and at 50°C., while Spielrein (18) has determined the isothermal invariant points, not very accurately, at 20°, 57°, and 97°C. At all temperatures, the solid phases occurring are ammonium sulphate, double salt, and either anhydrous lithium sulphate mixed with monohydrate or, more probably, solid solutions containing ammonium sulphate in excess of lithium sulphate. From an examination of the lithium sulphate corner of any of the isotherms, particularly that for 95°C., the uncertainty involved in defining the nature of the lithium sulphate solid phase is evident. The tie lines to the first branch of the isotherm shift progressively, without crossing, from the composition of the pure monohydrate to a point on the lithium sulphate – ammonium sulphate base corresponding to a solid phase containing about 10% by weight ammonium sulphate (at invariance). It is impossible to account for this as due to analytical error; it must represent solid solution; the same observation was made by Schreinemakers. On the other hand dehydration of monohydrate to anhydrous lithium sulphate is unlikely because of the very high transition temperature (3) of monohydrate to anhydrous form.

EXPERIMENTAL WORK

The main purpose of this work was the complete investigation of the isotherms at 0.1°, 71.8°, and 95.2°C. by the familiar "wetrest" method of Schreinemakers, with a view to the prediction of the transition temperature of the double salt. In order to complete the study of the system in a downwards temperature direction, the two ternary eutectics were determined by the method of thermal analysis. Other points arose in the course of the investigation, viz.:

The checking of the two binary eutectic temperatures and compositions by thermal analysis.

The investigation of Friend's contention (6) that a higher hydrate than the monohydrate exists at low temperatures; the dilatometer was used for this.

Finally, since the forms of our isotherms indicated that the transition temperature from double salt to constituent single salts was approached by lowering the temperature (of course, it cannot be realized because the system freezes), it was decided to confirm this thermodynamically by determining the enthalpies of solution of single salts and of double salt and hence

obtaining the enthalpy of formation of double salt from single salts:

$$Li_2SO_4 \cdot H_2O + (NH_4)_2SO_4 \rightarrow Li_2SO_4 \cdot (NH_4)_2SO_4 + H_2O.$$

Le Chatelier's principle then confirms our deduction.

Preparation and Purification of Materials

B.D.H. Analar lithium sulphate, containing only negligible impurities, was used without recrystallization. Baker's C.P. Analyzed ammonium sulphate, free from pyridine, was recrystallized once. The double salt was prepared by adding the two sulphates in equimolecular proportion to water until the hot solution was saturated. Nicol's "Mercury Metal" and Analar grade chloroform were used for the calibration of the thermocouple and were redistilled before use.

Method of Analysis

Total sulphate and ammonia were determined and the lithium obtained by difference. Despite extensive criticism of the method (1, 8) sulphate was determined by the time-honored gravimetric method of precipitation as barium sulphate. Following the procedure of Kolthoff and Sandell (9) an accuracy of better than 0.5% was consistently obtained and this was sufficient for our purposes.

The determination of the ammonia content was made by steam distillation of a basic solution. The distillate was absorbed in a boric acid solution of approximately 4% strength, following the method outlined in Pierce and Haenisch (12) and originally proposed by Winkler (19).

Calibration of Thermocouple

For the thermal analysis work at low temperature, an iron constantan thermocouple was used, the e.m.f. being determined on a sensitive potentiometer. The method of calibration was that of Rosser and Dahl (14). The fixed points used were: freezing point of mercury (−38.9°C.), freezing point of chloroform (−63.5°C.), sublimation point of carbon dioxide (−78.5°C.), and the melting point of ice; the hot junction was kept in melting ice.

Calorimetric Measurements

Determinations of enthalpies of solution were made in order to find the enthalpy of formation of the double salt. An electrical calorimeter was used with ordinary precautions; for example, the power input was determined as the fall of potential over a standard resistance and voltage determinations were made on a potentiometer; radiation corrections were applied. The accuracy of the results is sufficient for our purpose, which was merely to demonstrate that the formation of the double salt from the constituent salts is an endothermal process, but is not to be compared with the accuracy required in modern thermochemical work.

RESULTS

The Binary Eutectic Ammonium Sulphate – Ice

Previous workers (7, 13, 16, 15, 2, 10) give the eutectic conditions as:—composition, 38.40 – 39.90% $(NH_4)_2SO_4$, temperature −18.34°C. to −19.5°C.

We redetermined these values by thermal analysis. A solution of approximately eutectic composition was cooled in dry ice, two air jackets being used to decrease the rate of cooling. The solution was stirred mechanically throughout. When the thermocouple potential became constant, a sample of solution was removed through a (previously chilled) fritted glass filter, for analysis. As the mean of two experiments, we find eutectic temperature −19.5°C., eutectic composition 39.2% $(NH_4)_2SO_4$.

Binary Eutectic Lithium Sulphate Monohydrate – Water

According to Campbell (3) the eutectic temperature for this is −23.0°C. and the eutectic composition 27.9% anhydrous lithium sulphate. The eutectic composition was obtained by extrapolation of Friend's (6) solubility curve and Campbell's ice-line. We attempted to check these data in the same manner that we used to check the eutectic of the ammonium sulphate – water system. A mixture of 27.9 gm. anhydrous lithium sulphate and 72.1 gm. of water was prepared. With steady cooling, a constant e.m.f. value was, however, never obtained. Since it was possible that the rate of cooling might have been too rapid, this rate was lessened in a repeat experiment, but again no constant e.m.f. value was obtained. In a second repeat of the experiment, excess of lithium sulphate was added to the initial solution and a better system of stirring devised, but no e.m.f. value was obtained which could be interpreted as being the eutectic temperature. Samples of clear solution which were withdrawn at −23.0°C. were found upon analysis to contain 26.1% lithium sulphate and this is in fair agreement with Campbell's result. We are unable to state why a direct experimental determination of the eutectic seems to be impossible, unless it be connected with the peculiar re-entrant form of the solubility curve, just above the eutectic temperature.

Hydrates of Lithium Sulphate

To investigate further Friend's (6) statement that a higher hydrate of lithium sulphate than monohydrate exists at low temperatures and Campbell's (3) contrary conclusions that no such higher hydrate exists, a dilatometer was used. The bulb of the dilatometer was charged with wet monohydrate and toluene was the indicator fluid. The temperature of the dilatometer was lowered progressively from −0.5°C. to −17.9°C. The plot of toluene level against temperature was a perfectly straight line, indicating the absence of any transition. Since it was possible that time had not been allowed for the conversion to take place, the bulb of the dilatometer was now immersed in a large quantity of ice and sodium chloride mixture and cathetometer readings of the toluene level taken until a constant reading was obtained. The temperature was noted (−21°C.) and the assemblage allowed to stand for 24 hr. No change was observed in the toluene level at the expiration of the period. Hence a higher hydrate did not form under these experimental conditions. Finally, samples of moistened lithium sulphate monohydrate were sealed in glass containers and preserved in ice – sodium chloride mixtures for periods ranging from 24 to 72 hr. No visible change in crystal structure could be observed and the samples still appeared wet.

The Ternary Eutectics

In a ternary system consisting of two salts and water and forming one double salt (congruently saturating), there are two eutectics involving ice as one phase. These ternary eutectics represent completely invariant systems (F = O), since five phases, three of them solid, are in equilibrium. The solid phases in equilibrium at the two eutectics are, respectively: (1) ammonium sulphate, double salt, ice and (2) lithium sulphate monohydrate, double salt, ice.

The temperatures and compositions of these two eutectics were determined by thermal analysis. The procedure was similar to that employed in investigating the two binary eutectics. Starting from weighed amounts of the respective binary eutectic solutions, weighed quantities of the second salt were added and the mixture submitted to thermal analysis. Provided the original mixture lay exactly in the eutectic trough, the first point of inflection on the cooling curve represented the so-called freezing point, that is, the temperature at which simultaneous deposition of ice and one salt occurred. If the composition were slightly off the trough composition, a preliminary point of inflection would indicate prior separation of either ice or salt singly, followed by simultaneous crystallization, but such points on the cooling curve are easily interpreted. The composition of the first (ternary eutectic) solution was determined by withdrawing a sample for analysis. Theoretically, any initial solution containing the three components should, on continued cooling, give a final solution corresponding to one or other of the (ternary) eutectic compositions. In practice, however, it was found that it was necessary to have initial solutions whose compositions were rather close to the eutectic composition, in order to obtain the true eutectic composition on cooling. In addition to the two binary eutectic troughs, the two ternary eutectics are joined by a section of a surface, having a temperature maximum representing the pseudobinary eutectic ice – double salt. Three points on this curve were obtained by cooling a solution of double salt, with or without slight excess of lithium sulphate or of ammonium sulphate. The data obtained are reproduced in Table I.

TABLE I

THE TERNARY EUTECTIC CURVES

Temperature	$\%(NH_4)_2SO_4$	$\%Li_2SO_4$
−19.5	39.2	0.0
−22.5	37.0	5.1
−27.0	33.2	10.5*
−26.0	23.3	16.2
−26.0	20.4	18.8
−23.0	18.3	20.8
−30.0	10.6	27.4*
−24.0	6.0	26.8
−23.0	0.0	27.9

**These determinations represent the two eutectic temperatures and compositions. They are mean values.*

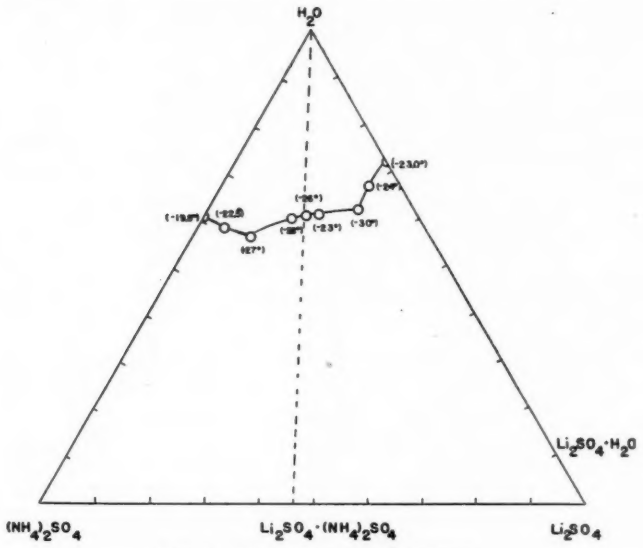

FIG. 1. The ternary eutectic curves.

The above data are plotted in Fig. 1. From an examination of Table I and Fig. 1, the eutectics are to be deduced as follows: Eutectic 1. Solid phases: ammonium sulphate, double salt, ice; temperature − 27°C.; composition: 33.2% $(NH_4)_2SO_4$, 10.5% Li_2SO_4. Eutectic 2. Solid phases: lithium sulphate monohydrate, double salt, ice; temperature − 30.0°C.; composition: 10.6% $(NH_4)_2SO_4$, 27.4% Li_2SO_4.

TABLE II
ISOTHERM FOR 0.10° (± 0.05°)

No.	Solution		Wet residue		Nature of the solid phase
	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	
1	0.0	26.5	....	....	$Li_2SO_4 \cdot H_2O$
2	6.4	25.4	2.3	64.4	"
3	6.2	25.2	1.0	78.8	"
4	9.7	24.4	14.1	51.0	$Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot (NH_4)_2SO_4$
5	9.8	24.3	25.3	35.7	"
6	14.1	20.9	38.0	36.1	$Li_2SO_4 \cdot (NH_4)_2SO_4$
7	18.4	17.4	38.1	33.9	"
8	18.5	17.3	40.0	34.0	"
9	20.5	16.0	40.6	34.4	"
10	24.8	13.8	41.6	32.2	"
11	36.1	8.4	78.6	7.6	$Li_2SO_4 \cdot (NH_4)_2SO_4$ and $(NH_4)_2SO_4$
12	36.2	8.1	82.1	4.1	"
13	37.7	5.3	84.5	2.1	$(NH_4)_2SO_4$
14	38.7	3.5	82.4	1.4	"
15	41.8	0.0	....	....	"

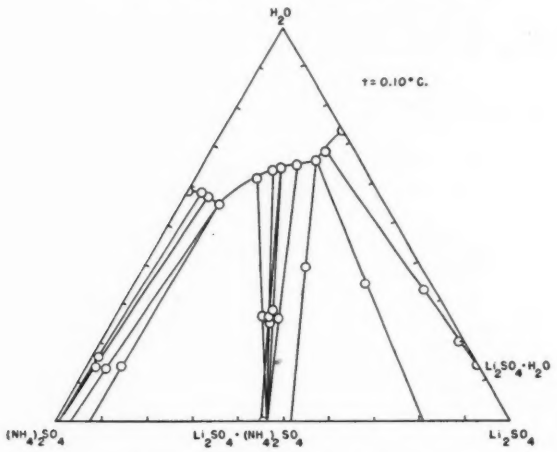

FIG. 2. The 0.1°C. isotherm.

The 0.1°, 71.8°, and 95.2°C. Isotherms of the Ternary System

The technique of this kind of work has been too frequently described to require discussion here. For 0.1°C., the thermostat, containing kerosene, consisted of a large glass cylinder placed in an outer tank which also contained kerosene. The outer bath was cooled by a thermostatically controlled refrigerating coil. The inner thermostat, which was electrically controlled, was heated by a light bulb. For the other temperatures, the thermostat was of the usual type. The results in weight per cent are given in Tables II, III, and IV. The corresponding equilibrium diagrams are represented in Figs. 2, 3, and 4.

TABLE III

ISOTHERM FOR 71.8° ± 0.10°C.

No.	Solution		Wet residue		Nature of the solid phase
	Wt. % $(NH_4)_2SO_4$	Wt. % Li_2SO_4	Wt. % $(NH_4)_2SO_4$	Wt. % Li_2SO_4	
1	0.0	24.2	....	....	$Li_2SO_4 \cdot H_2O$
2	2.4	23.5	1.2	66.3	"
3	5.6	23.1	2.1	62.5	"
4	12.1	21.8	8.5	59.6	$Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot (NH_4)_2SO_4$
5	20.1	17.1	48.2	40.0	$Li_2SO_4 \cdot (NH_4)_2SO_4$
6	20.4	17.2	42.4	35.2	"
7	25.6	14.2	44.9	35.0	"
8	32.1	10.5	46.8	35.4	"
9	44.9	5.2	66.2	19.3	$Li_2SO_4 \cdot (NH_4)_2SO_4$ and $(NH_4)_2SO_4$
10	45.1	5.5	76.8	2.7	$(NH_4)_2SO_4$
11	47.9	0.0	....	....	"

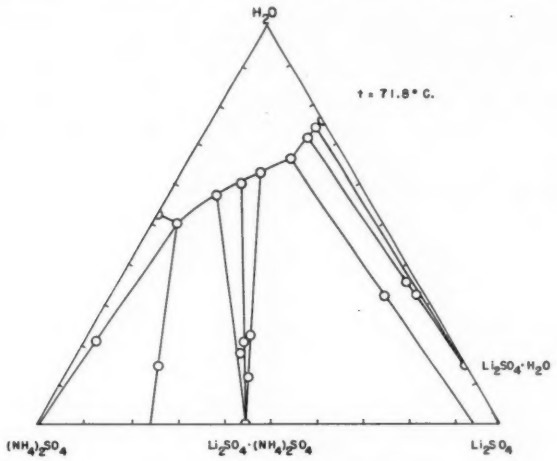

FIG. 3. The 71.8°C. isotherm.

TABLE IV
ISOTHERM FOR 95.2°C..

No.	Solution		Wet residue		Nature of solid phase
	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	
1	0.0	24.12	....	....	$Li_2SO_4 \cdot H_2O$
2	0.69	24.70	0.36	78.90	Solid solution in $Li_2SO_4 \cdot H_2O$
3	4.65	23.09	3.35	66.60	"
4	9.34	21.72	9.13	58.76	"
5	15.89	20.46	34.36	38.99	Sat'd. solid sol'n. in $Li_2SO_4 \cdot H_2O$ + $Li_2SO_4(NH_4)_2SO_4$
5a	15.91	20.62	22.96	50.65	"
6	21.11	16.37	44.47	36.81	$Li_2SO_4 \cdot (NH_4)_2SO_4$
7	40.03	6.73	47.50	26.66	"
8	47.98	3.67	68.05	19.94	$Li_2SO_4 \cdot (NH_4)_2SO_4$ + $(NH_4)_2SO_4$
9	48.67	3.04	83.10	1.00	$(NH_4)_2SO_4$
10	50.87	0.0	....	....	$(NH_4)_2SO_4$

Heats of Solution

The results for the molal enthalpies of solution of ammonium sulphate, of lithium sulphate monohydrate, and of double salt, in water, at various concentrations, and of ammonium sulphate in solutions containing equivalent quantities of lithium sulphate (all at room temperature), are given in Table V. In accordance with thermodynamic notation, a positive value of ΔH means that during the process of solution the solution absorbs heat from the surroundings.

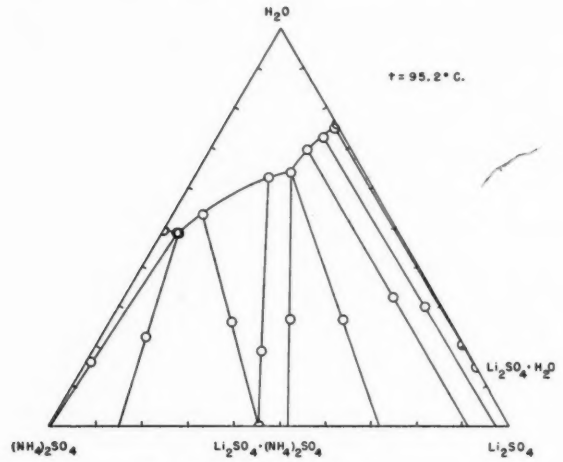

Fig. 4. The 95.2°C. isotherm.

TABLE V
ENTHALPIES OF SOLUTION AT ROOM TEMPERATURE (24°C.)

$Li_2SO_4 \cdot H_2O$ in water		$(NH_4)_2SO_4$ in water	
Molality	ΔH_1 (kcal.)	Molality	ΔH (kcal.)
0.274	−2.34	0.599	3.09
0.546	−2.40	1.16	2.83
0.796	−2.46	1.74	2.69
1.08	−2.63	2.31	2.59
1.35	−2.79	2.89	2.44
1.61	−2.88	4.41	2.33
1.86	−2.84	5.15	2.41
2.12	−2.63	6.00	2.39
2.37	−2.47		
2.63	−2.34		
$(NH_4)_2SO_4$ in equiv. Li_2SO_4		Double salt in water	
Molality	ΔH_2 (kcal.)	Molality	ΔH_4
0.341	2.91	0.165	−2.40
0.685	2.80	0.330	−2.59
1.13	2.63	0.495	−2.57
1.37	2.47	0.660	−2.41
1.71	2.46	0.825	−2.29
2.05	2.39	0.990	−2.15
2.39	2.39	1.16	−2.04
		1.32	−1.93
		1.63	−1.83
		1.81	−1.74
		1.98	−1.61
		2.17	−1.51

DISCUSSION OF RESULTS

The values of composition and of temperature for the binary eutectic ammonium sulphate – ice agree well with the literature data but the direct

experimental check of the corresponding data for the eutectic lithium sulphate monohydrate – ice is somewhat uncertain. In one of the experiments, the cooling curve exhibited a change of slope at − 23°C. and a sample of solution withdrawn at this temperature contained 26.1% Li_2SO_4, in rough agreement with Campbell's interpolated value of 27.9%. The cooling curve did not, however, show a definite halt and thus the figure is at best uncertain. The ternary eutectic curves of Table I and Fig. 1 tend to substantiate Campbell's result; the right hand eutectic curve of Fig. 1 includes Campbell's value for the binary eutectic smoothly: the depression by 1° of the binary eutectic temperature seems reasonable. If reference is made to the equilibrium diagram of the system $Li_2SO_4 - H_2O$, given in Campbell's paper (3), the reason for our inability to obtain a eutectic halt may seem to lie in the peculiar form of the freezing and solubility curves in the neighborhood of this eutectic.

We have been unable to find any positive evidence for the existence of Friend's (6) higher hydrate of lithium sulphate.

Examination of the solubility isotherms, both those of Schreinemakers and our own, shows that at all temperatures from 0°C. to 95°C., the double salt is stable and congruently saturating. Only one double salt is formed, viz. $Li_2SO_4 \cdot (NH_4)_2SO_4$. All isotherms indicate a limited solid solubility of ammonium sulphate in lithium sulphate (presumably the monohydrate). There may also be a slight solubility of lithium sulphate in double salt but there is no detectable solubility of double salt in ammonium sulphate or of ammonium sulphate in double salt. This leads us to suppose that the lattices of lithium sulphate monohydrate and of the double salt are similar, but that no such similarity exists between the lattices of double salt and of ammonium sulphate. The question might merit a crystallographic and X-ray study.

The data of the isotherms (our own and Schreinemakers') were recalculated in the form: weight ammonium sulphate and weight (anhydrous) lithium sulphate per 100 gm. water. These were expressed graphically in Fig. 5. The comparative lengths of the intermediate curve, on which double salt is stable, indicate the relative regions of stability of the double salt. If these are measured as straight lines, the following figures are obtained, (on the original diagram):

0°C.	14 cm.
30°C.	15 cm.
50°C.	17 cm.
71.8°C.	19.5 cm.
95°C.	20 cm.

Such measurements are, of course, very rough but they show beyond a doubt that the (hypothetical) transition temperature of the double salt is approached by lowering the temperature. (Cf. the behavior of the corresponding sodium ammonium double salt, which is quite different.)

It therefore appears, since the stability of the lithium ammonium double salt increases with rising temperature, that it is an endothermal compound, that is, that in the process

$$Li_2SO_4 \cdot H_2O + (NH_4)_2SO_4 \rightarrow Li_2SO_4 \cdot (NH_4)_2SO_4 + H_2O$$

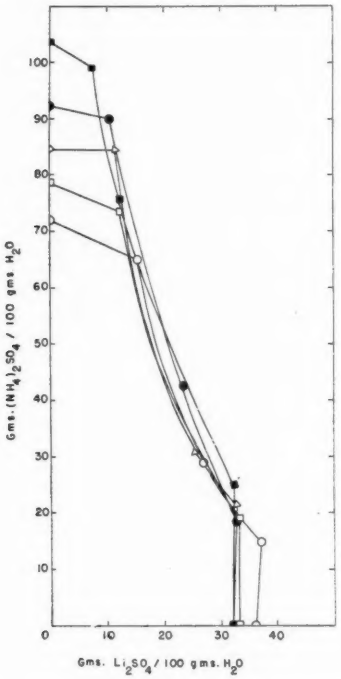

FIG. 5. The isotherms on rectangular co-ordinates.

○	0.1°C.	C. Mc. K.
□	30°	Schreinemakers
△	50°	Schreinemakers
●	71.8°	C. Mc. K.
■	95.2°	C. Mc. K.

heat is absorbed, and therefore ΔH is positive. If we give the symbol ΔH_3 to the enthalpy of the above process and indicate by ΔH_1 the enthalpy of the process

$$Li_2SO_4 \cdot H_2O + Aq \rightarrow Li_2SO_4 \cdot Aq,$$

by ΔH_2 that of the process

$$(NH_4)_2SO_4 + Aq \rightarrow (NH_4)_2SO_4 \cdot Aq,$$

and by ΔH_4 that of the process

$$(NH_4)_2SO_4 \cdot Li_2SO_4 + Aq \rightarrow (NH_4)_2SO_4 \cdot Li_2SO_4 \cdot Aq,$$

we obtain ΔH_3 as

$$\Delta H_3 = \Delta H_1 + \Delta H_2 - \Delta H_4,$$

provided that we use for ΔH_2, not the enthalpy of solution of $(NH_4)_2SO_4$ in pure water, but that in a solution containing equivalent quantities of lithium sulphate. The following figures are obtained.

Concentration of solution, molal	ΔH_3, kcal.
0.2	3.27
0.4	3.07
0.6	2.84
0.8	2.58
1.0	2.24
1.2	2.03
1.4	1.62
1.6	1.63
1.8	1.28
2.0	1.27
2.2 (saturated)	1.29

The levelling off to constancy as saturation is approached shows that the true ΔH of formation of the double salt is 1.28 ± 0.01 kcal. This positive value accounts for the double salt having a downwards transition temperature.

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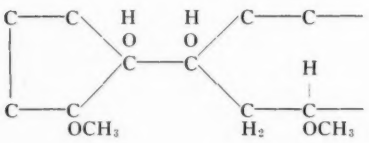
LYCOCTONINE: ACID CATALYZED REARRANGEMENTS[1]

By O. E. Edwards, Léo Marion, and R. A. McIvor[2]

ABSTRACT

The lactam derived from the alkaloid lycoctonine has been shown to undergo rearrangement when heated with mineral acids. A ketone, anhydrolycoctonam, is formed first by pinacolic dehydration. This ketone then undergoes elimination of the elements of methyl alcohol, and hydrolysis of a methoxyl to give lycoctamone, an α–β unsaturated ketone containing a new tertiary hydroxyl. Reactions of lycoctamone and its reduction products are described and discussed.

The alkaloid lycoctonine, for which the expanded formula $C_{19}H_{21}(OH)_3(OCH_3)_4NC_2H_5$ can be written, is most probably a saturated hexacyclic base. Evidence has been presented in the preceding papers (4,5) for the presence in the alkaloid of the systems



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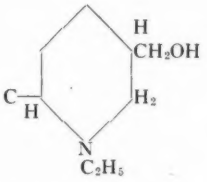
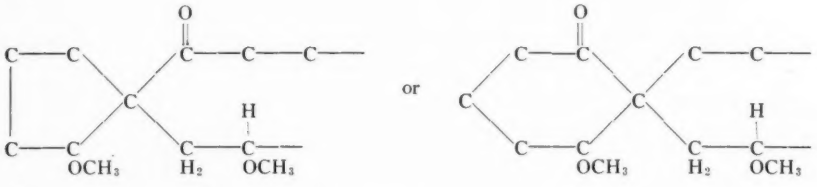


It was shown that the glycol system can undergo a ready pinacolic dehydration. For example, the lactam derived from lycoctonine, lycoctonam, gives the ketone, anhydrolycoctonam, with loss of one molecule of water. Since anhydrolycoctonam only gives a faint reaction with hot Fehling's solution, and only slowly gives a weak Tollens' test, it is unlikely that it has a methoxyl α to the carbonyl. It is stable to alkali, hence has no methoxyl β to the carbonyl which can be readily eliminated. Thus the two most probable partial structures for the 'anhydro' compounds derivable from the above structure are:



I or II

Anhydro Compound

Several arguments can be advanced as to the relative likelihood of I and II. The hydroxyl on the cyclopentane ring in the glycol system, being α to a

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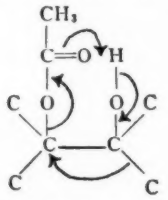
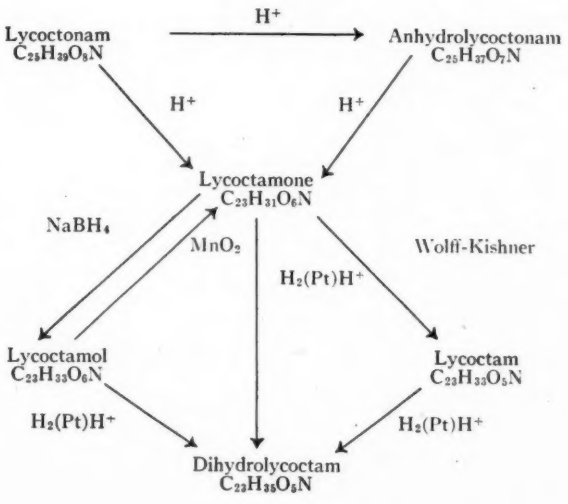
methoxyl, should be less basic than the one on the larger ring. Thus on this basis alone, the pinacolic dehydration would be expected to give II. However, on the basis of the considerations of Brown and co-workers (3) it appears likely that the hydroxyl on the five-membered ring would be more readily eliminated, giving the more stable cyclopentyl carbonium ion. This would give rise to I on rearrangement. The same conclusion is reached on consideration of the pyrolysis of des(oxymethylene)-lycoctonam monoacetate (4). Since the cyclopentanone carbonyl in the diketones derived from lycoctonine derivatives is much less hindered than that on the larger ring (5), it is reasonable to suppose that the same relative hindrance exists for the hydroxyls in the parent glycol. Hence the above acetate should involve the hydroxyl on the five-membered ring. Since the pyrolysis most likely proceeds as shown,



the product would again be I, making this seem the more likely possibility.

Anhydrolycoctonam could be recovered unchanged after attempted Wolff-Kishner reduction, hence the carbonyl is very hindered. In concordance with this, the carbonyl is only slowly reduced by sodium borohydride. The hydroxyl derived from the ketone in this reduction could be acetylated readily, however, giving an acetate which did not lose acetic acid readily at 290°. These observations, and the fact that the ketone was inert to selenium dioxide in

FLOWSHEET



refluxing acetic acid, suggest that the other carbon α to the carbonyl is tertiary or perhaps quaternary.

On more vigorous treatment with acid, lycoctonam and anhydrolycoctonam undergo extensive change. One methoxyl is hydrolyzed to a tertiary hydroxyl

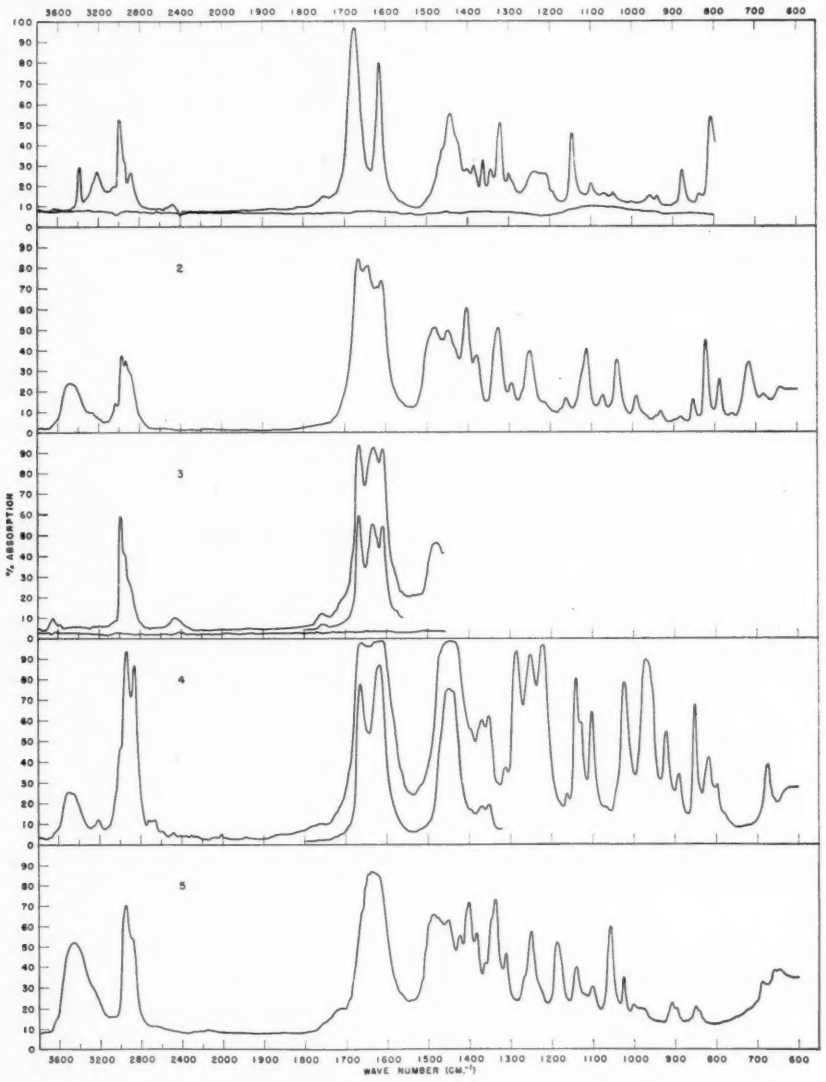


FIG. 1. Infrared spectra (nujol mulls): 1. Dihydroanhydrolycoctonam diacetate. 2. Lycoctamone monoacetate. 3. Lycoctamol monoacetate. 4. Lycoctam monoacetate. 5. Dihydrolycoctam monoacetate.

(highly hindered and inert to chromic acid), and a second methoxyl is eliminated as methyl alcohol. The product is an α–β unsaturated ketone ($\lambda\lambda_{max}$ 245 mμ, log ϵ 4.01 and 310 mμ, log ϵ 2.20) of formula $C_{23}H_{31}O_6N$. The name lycoctamone has been chosen to designate this important degradation product. The reactions which have been used to elucidate the changes in the formation of lycoctamone are indicated on the flowsheet.

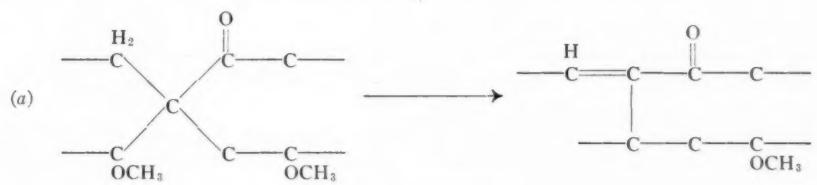
It is evident that anhydrolycoctonam is an intermediate in the formation of lycoctamone, and that information gathered about the environment of the carbonyl in the former may be used in the interpretation of the mode of formation of the latter.

Lycoctamone and dihydrolycoctam form exceptionally stable monohydrates, and no very satisfactory analyses have been obtained for the anhydrous compounds. The acetates, however, gave good analyses.

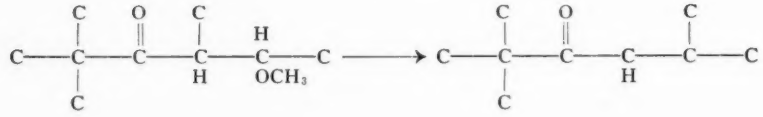
Lycoctamone still contains a readily acetylated hydroxyl, presumably the original primary one. The position of the short wave length ultraviolet maximum indicates, if the Woodward-Fieser (6) rules are obeyed, that the α–β unsaturated ketone is trisubstituted endocyclic (calc. λ_{max}249 mμ) or disubstituted exocyclic (calc. λ_{max}242-244 mμ). The fairly rapid catalytic reduction of the double bond argues in favor of the disubstituted possibility. Additional support for this comes from the infrared spectrum. Lycoctamone, lycoctamol, and lycoctam (see flowsheet) have what is probably a CH-bending band near 830 cm.$^{-1}$ (Fig. 1) which is absent in dihydrolycoctam. A band in this position is characteristic of a trialkyl substituted double[3] bond (9).

Lycoctamone is inert to bismuth oxide in boiling acetic acid (8) and to periodic acid, hence it is not an α-ketol. In contrast to the situation in anhydrolycoctonam, the carbonyl in lycoctamone is readily reduced by sodium borohydride to the allyl alcohol lycoctamol, and by the Wolff-Kishner method to lycoctam. This suggests that some of the hindrance of the carbonyl has been removed by carbon migration.

A plausible explanation of the formation of lycoctamone is that a methoxyl β to the carbonyl in anhydrolycoctonam is eliminated with an attendant Wagner-Meerwein shift to give the α–β unsaturated ketone. Two types of situation can be envisaged which would favor such a change. Either a methoxyl separated from the carbonyl by a quaternary carbon is involved as in (*a*), or a methoxyl β to the carbonyl, having the wrong orientation for easy elimination with an α-hydrogen, is eliminated as in (*b*).

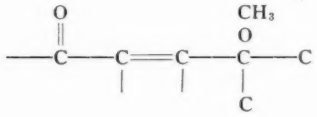


[3]*Note the difference in nomenclature. A trisubstituted double bond corresponds to a disubstituted α–β unsaturated ketone.*

(*b*) 

The arrangement of atoms necessary for (*a*) is present in partial structures I and II for anhydrolycoctonam. However, a detailed consideration of the various possibilities will be deferred until more evidence is available on the substitution near the carbonyl in lycoctamone and anhydrolycoctonam.

Since in the products of periodate cleavage of the glycol system in lycoctonam the methoxyls are resistant to hydrolysis (see experimental section and reference 5) it is clear that during the formation of lycoctamone a methoxyl becomes unusually labile. This lability would be readily explained if the methoxyl were located as shown, making it a vinylogue of an α-methoxy ketone.



The hydrogenolysis of lycoctamone and lycoctamol has many parallels (7,10). Although the new tertiary hydroxyl is also in an allylic position if the above conclusions are correct, it does not readily undergo hydrogenolysis. The uptake of hydrogen by lycoctamol was consistently over two moles, but the product consisted mainly of lycoctam, in which only the secondary hydroxyl was eliminated.

Considerable information is now available about two or perhaps three of the methoxy groups of lycoctonine. The conclusions as to the degree of substitution of the double bonds in lycoctamone and the desmethanol diketones (5) will have to be checked by oxidation studies before a choice can be made among the various possible partial structures for lycoctamone.

EXPERIMENTAL

The activity of the alumina is cited using the scale proposed by Brockmann (2). Melting points are corrected to within one degree. Rotations were determined in absolute ethanol, the cited temperature being that of the room. The ultraviolet spectra were determined on solutions in 95% ethanol using a Beckman D.U. spectrophotometer. Infrared spectra were determined on a Perkin-Elmer model 21 double beam spectrophotometer.

Anhydrolycoctonam—Attempted Reactions

(*a*) The compound was recovered unchanged after attempted Wolff-Kishner reduction at 200° in triethylene glycol.

(*b*) Over 90% of the compound was recovered after 20 hr. reflux with selenium dioxide (1 mole) in acetic acid.

(*c*) Anhydrolycoctonam darkened Tollens' solution slightly in 30 min. at room temperature. It gave a tiny red precipitate with Fehling's solution at 100° in five minutes with little change after a further five minutes of heating.

Dihydroanhydrolycoctonam Diacetate

Anhydrolycoctonam (116 mgm.) was dissolved in 2 cc. of methanol and 1 cc. of 10% aqueous sodium borohydride solution added. After standing for 22 hr. at room temperature, the solution was refluxed for 35 min. The excess borohydride was decomposed with acid and the product extracted into chloroform. The 125 mgm. recovered from the chloroform could not be induced to crystallize. It was acetylated overnight with acetic anhydride – pyridine. The 145 mgm. of neutral product was dissolved in ether and petroleum ether added, giving 83 mgm. of crude crystals. After one recrystallization this melted at 167–172°. After purification by chromatography on alumina and recrystallization the diacetate was obtained as needles, m.p. 174–177°. $[\alpha]_D^{25}$ 33 ± 1° (*c* = 1.8). Found: C, 63.81; H, 7.85. Calc. for $C_{29}H_{43}O_9N$: C, 63.37; H, 7.89. Infrared spectrum (Fig. 1): Bands at 1636 and 1738 cm^{-1}.

When anhydrolycoctonam was treated with sodium borohydride solution for 15 min. at room temp. 81% of the compound was recovered in a slightly impure condition (m.p. 142°).

Desmethanolsecolycoctonam Diketone—Attempted Hydrolysis

A solution of 44 mgm. of the ketone in 2 cc. of 6 *N* sulphuric acid was refluxed vigorously for 3.5 hr. The product was extracted with methylene chloride, and the solvent removed. The residue (45 mgm.) crystallized from ether containing a little acetone, giving 34 mgm. of starting material.

Lycoctamone

(*a*) Lycoctonam hydrate (500 mgm.) in 8 cc. of 12 *N* sulphuric acid was heated at 100° for two hours. The solution was cooled, partially neutralized with sodium carbonate, and extracted with chloroform. The 440 mgm. of brown residue from the chloroform solution crystallized when water was added, giving 260 mgm. of tan crystals, m.p. 205–215°. This was best purified by adsorption from 50% benzene–chloroform on 20 times its weight of neutral alumina, activity 4, and elution with this solvent mixture and with chloroform. The eluates, crystallized from aqueous methanol, melted at 218–225° (immersed at 200°). After three recrystallizations from concentrated methanol solution the colorless prisms melted at 221–225°. After drying 24 hr. at 110° over phosphorus pentoxide *in vacuo* it had $[\alpha]_D^{20}$ 274 ± 2° (*c* = 2.0). Found: C, 63.70, 64.01; H, 7.64, 7.81; OCH_3, 15.43, 14.91. Calc. for $C_{23}H_{31}O_6N \cdot H_2O$: C, 63.43; H, 7.64; 2 OCH_3, 14.25. Ultraviolet spectrum: λ_{min}230 mμ (3.95); λ_{max} 245 mμ (4.01); λ_{min} 300 mμ (2.18); λ_{max} 310 mμ (2.20). A sample of lycoctamone hydrate was sublimed at 180° under 5×10^{-4} mm. It then melted at 217–223°, $[\alpha]_D^{22}$ 258 ± 4° (*c* = 1.3). Found: C, 65.97, 65.54; H, 8.15, 8.07; Calc. for $C_{23}H_{31}O_6N$: C, 66.16; H, 7.48. Infrared spectrum (mull): Bands at 1610 (lactam) and 1661 $cm.^{-1}$ (ketone) and 3550, 3370, and 3260 $cm.^{-1}$ (hydroxyls).

(*b*) Anhydrolycoctonam (40 mgm.) in 2 cc. of 6 *N* sulphuric acid was refluxed gently in a carbon dioxide atmosphere for five hours. The solution was cooled, neutralized with ammonia, and extracted with chloroform. The 34 mgm. of product crystallized when water was added, giving 25 mgm., m.p. 210–220°. This did not depress the melting point of the product from (*a*).

Lycoctamone gave a black precipitate with Tollens' reagent at room temperature in 20 min. It only reduced Fehling's solution slightly after 15 min. at 100°. It was recovered unchanged after 70 hr. in an aqueous–methanol solution of periodic acid (approx. 0.2 molar) and it was not oxidized by bismuth oxide in refluxing acetic acid.

Lycoctamone Monoacetate

(*a*) Pure lycoctamone (108 mgm.) left at room temperature for 72 hr. with 2 cc. of acetic anhydride and 2 cc. of pyridine gave 114 mgm. of neutral acetate. This crystallized readily from acetone, giving 72 mgm., m.p. 235–242°. The compound purified by chromatography on alumina (activity 4) and recrystallization softened at 235° and melted by 242° (immersed at 215°). $[\alpha]_D$ 192 ± 2° (c = 2.6). Found: C, 65.26, 65.56; H, 7.37, 7.18; N, 3.04; OCH_3, 13.22. Calc. for $C_{25}H_{33}O_7N$: C, 65.34; H, 7.24; N, 3.05; 2 OCH_3, 13.51. Ultraviolet spectrum: λ_{min} 231 mμ (3.94); λ_{max} 245 mμ (3.98). Infrared spectrum (Fig. 1): Bands at 3425, 1741, 1670, and 1623 cm^{-1}.

(*b*) Lycoctonam acetate (253 mgm.) in 20 cc. of glacial acetic acid containing 0.02 cc. of conc. sulphuric acid was heated at 105 ± 2° for 1.5 hr. Two hundred milligrams of sodium carbonate was added, then the solution taken to near dryness under reduced pressure. The residue was taken up in chloroform, washed with sodium carbonate solution, dried, and evaporated to a volume of 5 cc. Ten cubic centimeters of dry benzene was added, and the compound adsorbed from this onto 5 gm. of neutral alumina activity 3. The products were eluted rapidly with 50% benzene–chloroform. The first 84 mgm. crystallized readily from ether, giving 51 mgm. of crude anhydrolycoctonam acetate. The next 117 mgm. proved to be quite pure lycoctamone acetate, m.p. 242°. The material eluted by chloroform and methanol in chloroform did not crystallize readily.

At temperatures around 115° with similar reagent mixtures the conversion to lycoctamone acetate was more complete, yields of up to 80% on a weight basis being obtained.

Lycoctamone acetate was saponified readily at room temperature by potassium hydroxide in methanol. The recovered lycoctamone melted over a range up to 220°. A purer product was obtained by saponification at room temperature with aqueous methanol containing mineral acid (1 cc. of conc. sulphuric acid in 6 cc. of 50% aqueous methanol).

Lycoctamol

Sodium borohydride (30 mgm.) was added to a solution of 52 mgm. of lycoctamone in 2 cc. of 50% aqueous methanol. After 30 min. the excess borohydride was decomposed by addition of dilute sulphuric acid, and the solution extracted with six 4 cc. portions of chloroform. The 52 mgm. of product crystallized readily from ethyl acetate giving 37 mgm., m.p. 205°

and 9 mgm., m.p. up to 190°. After four recrystallizations from ethyl acetate the compound melted at 207–212° (immersed at 190°). It was dried at 100° over P_2O_5 *in vacuo* for 16 hr. $[\alpha]_D^{25}$ 212 ± 2° (c = 2.0). Found: C, 65.89, 66.03; H, 8.41, 8.38. Calc. for $C_{23}H_{33}O_6N$: C, 65.85; H, 7.93. The compound showed only end absorption in the ultraviolet. It appeared somewhat unstable. Freshly recrystallized samples dried at 100° for three to five hours *in vacuo* had rotation of 219 ± 3°, definitely higher than the sample heated for a longer period. Infrared spectrum (mull): Bands at 3350 and 1610 cm^{-1}.

A suspension of 0.4 gm. of active manganese dioxide (1) in a solution of 20 mgm. of lycoctamol in 3 cc. of dry benzene and 2 cc. of dry chloroform was agitated for 2.5 hr. The manganese dioxide was removed by filtration and the solid washed with chloroform. The combined filtrates contained 13 mgm. of product. This crystallized from ethyl acetate, giving 11 mgm., m.p. 224–228° which did not depress the melting point of lycoctamone.

Lycoctamol Monoacetate

Lycoctamone acetate (250 mgm.) was dissolved in 5 cc. of methanol, and 55 mgm. of sodium borohydride in 2 cc. of water was added. After five minutes the solution was acidified with dilute acid, and extracted with chloroform. The product crystallized nearly completely from acetone–ether, m.p. 170–214°. This was purified by chromatography on alumina giving 90 mgm., m.p. 214–218°. After three recrystallizations from acetone ether the compound melted at 216–218°. $[\alpha]_D^{20}$ 175 ± 2° (c = 2.7). Found: C, 65.13, 65.69; H, 7.91, 8.23. Calc. for $C_{25}H_{35}O_7N$: C, 65.05; H, 7.64. Infrared spectrum (mull) (Fig. 1): Bands at 3455, 3365, 1744, and 1623 cm^{-1}.

Lycoctamol Diacetate

When lycoctamol and lycoctamol monoacetate were acetylated overnight with acetic anhydride and pyridine they were converted to the same diacetate. This crystallized from ether – petroleum ether as fine needles, m.p. 177–180°. $[\alpha]_D^{18}$ 163 ± 2° (c = 1.84). Found: C, 63.87, 63.70; H, 7.11, 7.01; OCH_3, 12.45. Calc. for $C_{27}H_{37}O_8N$: C, 64.39; H, 7.41; 2 OCH_3, 12.32. Infrared spectrum (mull): Bands at 3435, 1743, 1625 cm^{-1}.

Lycoctam

Lycoctamone (45 mgm.), 1 cc. of triethylene glycol and 0.5 cc. of 85% hydrazine hydrate were heated in a bath at 130° for one hour. Eighty milligrams of potassium hydroxide was added, and the bath temperature raised over a period of one hour to 200°, allowing water and hydrazine to escape. The solution was then allowed to reflux at that bath temperature for four hours. It was cooled, diluted, and extracted with methylene chloride (5 cc. portions). Water was added to the 71 mgm. of oil extracted by the methylene chloride. Thirty milligrams of crystals were deposited which liquified between 100 and 105°, but did not run down in the tube until 125° was reached. On the hot stage this melted around 95°, slowly resolidified and melted at 157°. The compound after recrystallization from aqueous methanol had the form of feathery needles, m.p. 115–125°. This was dried for three hours at 100° *in vacuo* over P_2O_5, the melt cooled, pulverized, and redried for one hour $[\alpha]_D^{21}$ 160 ± 2° (c = 3.2). Found: C, 68.73; H, 8.43. Calc. for $C_{23}H_{33}O_5N$:

C, 68.46; H, 8.24. The ultraviolet spectrum showed only end absorption. Infrared spectrum (chloroform solution, 30 mgm. per ml., 0.1 mm. cell): Bands at 3575, 3400, 1615 cm^{-1}.

Lycoctam Monoacetate

Lycoctam (50 mgm.) was dissolved in 3 cc. of acetic anhydride and the solution left overnight at room temperature. The 54 mgm. of neutral acetate so obtained crystallized from ether on addition of petroleum ether. Crop 1, 16 mgm., m.p. 154–156°. Crop 2, 12 mgm., m.p. 140–158°. Crop 3, 6 mgm., softened at 100°, melted over a wide range. Products from preparations under varied conditions melted over ranges such as 151–159° and 153–162° after recrystallization. Found: C, 67.52; H, 8.16. Calc. for $C_{25}H_{35}O_6N$: C, 67.39; H, 7.92. Infrared spectrum: (Fig. 1): Bands at 3435, 3350, 1743, and 1620 cm^{-1}. Low melting material from the mother liquors from recrystallizations of the acetate (approx. 40 mgm.) was saponified readily by potassium hydroxide in methanol. The product gave crystals (29 mgm.) from aqueous methanol, m.p. 105–115°. This did not depress the m.p. of lycoctam.

Dihydrolycoctam

(*a*) Lycoctamone (27.1 mgm.) in 3 cc. of ethanol containing three drops of concentrated hydrochloric acid in the presence of platinum from 10.2 mgm. of platinum oxide (Adams') absorbed 4.43 cc. of hydrogen at 32°C. and 756 mm. pressure (mole ratio 2.84) in four hours. The catalyst was removed by filtration, the solvent evaporated under reduced pressure, and the residue taken up in 1 *N* sulphuric acid. Methylene chloride extraction of this solution yielded 27 mgm. of neutral product which crystallized from aqueous methanol giving 9 mgm., m.p. up to 170°. When recrystallized from ethyl acetate on addition of petroleum ether it melted at 179° and proved identical with the products from (*b*) and (*c*) (mixed m.p. and comparison of infrared spectra).

In similar hydrogenations varying the ratio of catalyst to compound and the concentration of hydrochloric acid, a molar uptake of hydrogen varying from 2.6 to 3 was observed. Yields of the crystalline product varied from 40 to 55% by weight of starting material.

(*b*) Lycoctamol (29 mgm.) in 3 cc. of ethanol containing three drops of concentrated hydrochloric acid in the presence of platinum from 10 mgm. of platinum oxide (Adams') absorbed 4.15 cc. of hydrogen at 26°C. under 754 mm. pressure (mole ratio 2.4). The product, isolated as in (*a*), crystallized readily from aqueous methanol giving 21 mgm., m.p. 173–178°.

(*c*) Lycoctam (16.8 mgm.) hydrogenated exactly as described in (*b*), absorbed 1.27 cc. of hydrogen at 27°C. under 763 mm. pressure (1.24 mole). The product crystallized from aqueous methanol, giving 13.5 mgm., m.p. 182°. After one recrystallization it melted at 180–185° and had an infrared spectrum identical with that of the product from (*a*).

Dihydrolycoctam, purified by chromatography on alumina of activity 4 (readily eluted by 50% chloroform–benzene) and recrystallized from aqueous methanol, had the form of needles, m.p. 182–184°. After drying seven hours

at 110° over P_2O_5 *in vacuo* it had $[\alpha]_D^{21}$ 85 ± 2° (c = 2.4). Found: C, 67.59; H, 8.59; OCH_3, 16.39. Infrared spectrum (mull): Bands at 3525, 3420, 1616 cm^{-1}. A sample was distilled at 170°, 5 × 10^{-4} mm. and the glass analyzed. Found: C, 67.48; H, 8.66. Calc. for $C_{23}H_{35}O_5N$: C, 68.12; H, 8.70; two OCH_3, 15.30.

Dihydrolycoctam Acetate

A solution of 79 mgm. of dihydrolycoctam in 1 cc. of acetic anhydride and 1 cc. of pyridine was left at room temperature for 45 hr. The mixture was taken to near dryness under reduced pressure and the residue taken up in chloroform. This solution was washed with dilute acid and with sodium carbonate solution, dried, and the solvent removed. The residue crystallized readily from ether giving 75 mgm., m.p. 198–204°, and some less pure material. After three recrystallizations from acetone–ether the compound softened at 202° and melted at 206°, $[\alpha]_D^{21}$ 33 ± 2° (c = 1.9). Found: C, 67.15, 67.05; H, 8.29, 8.46; OCH_3, 14.75; active hydrogen, 0.217. Calc. for $C_{25}H_{37}O_6N$: C, 67.09; H, 8.33; 2 OCH_3, 13.86; one active hydrogen, 0.225. Infrared spectrum (Fig. 1): Bands at 3475, 3425, 1742 and at 1635 and 1620 (split band) cm^{-1}.

Thirty seven milligrams of the acetate in 2 cc. of glacial acetic acid reduced 3 mgm. of chromium trioxide in five hours at room temperature, and 6 mgm. more when left overnight. The 40 mgm. of neutral product was taken up in ether, filtered from 2 mgm. of green residue, and concentrated. Crop 1: 18 mgm. m.p. 192–199°; crop 2, 4 mgm., m.p. 185–199°; crop 3, 3 mgm., m.p. 180–193°. These did not give a melting point depression when mixed with dihydrolycoctam acetate. The combined crystals when recrystallized from ether – petroleum ether melted at 200–204°.

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THE REACTIONS OF ACTIVE NITROGEN WITH THE BUTANES[1]

By R. A. Back and C. A. Winkler

ABSTRACT

The main product of the reactions of active nitrogen with *n*- and iso-butanes at 75° C. and 250° C. was hydrogen cyanide. Small amounts of C_2 hydrocarbons, mainly ethylene and acetylene, were produced in both reactions. Second order rate constants were calculated on the assumption that the reactive species in active nitrogen is atomic nitrogen, and that the initial attack of a nitrogen atom is the rate-controlling step. The activation energies were then estimated to be 3.6 kcal. and 3.1 kcal. and the probability factors 4.5×10^{-4} and 4.4×10^{-4}, for the *n*-butane and isobutane reactions respectively.

INTRODUCTION

Previous papers from this laboratory have described the reactions of active nitrogen with methane and ethane (1), propane (9), acetylene (13), ethylene (4, 14), propylene (12), and the butenes (3).

In the present paper are discussed the reactions of active nitrogen with *n*-butane and isobutane. The active species is assumed to be atomic nitrogen, for reasons indicated elsewhere (15).

EXPERIMENTAL

The apparatus was essentially similar to that described in previous papers. Reactions were studied in a fast flow system at a pressure of 1.34 mm. Hg. Active nitrogen was produced by a condensed discharge.

Condensable reaction products were separated into three fractions in a low temperature still of the type described by LeRoy (6). Ethane and ethylene were distilled at −170° C., and acetylene, propane, and propylene at −147° C. Each fraction was analyzed for total unsaturation, using conventional absorption technique (8, 2).

The third fraction, distilled at −30° C., contained hydrogen cyanide and butane. It was condensed into a large calibrated volume, warmed to room temperature, and the pressure recorded. By keeping the trap clean to avoid traces of water, and by never exceeding a total gas pressure of 400 mm. Hg, the hydrogen cyanide could be completely vaporized without appreciable polymer formation. The hydrogen cyanide and butane were then condensed into a detachable trap on top of 10 ml. of 1 *N* potassium hydroxide solution which was previously degassed and frozen in liquid nitrogen. The trap was removed under vacuum, and the bottom immersed in boiling water. In this way the solution melted first and the hydrogen cyanide dissolved before it could melt and polymerize. The cyanide content of the solution was determined by a silver nitrate titration, and the butane determined by difference.

Samples of noncondensable gas were removed from the flow system during

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the reactions with a Toepler pump located beyond the liquid nitrogen traps, and were analyzed for N_2, H_2, and CH_4 with a mass spectrometer.*

Experiments were made at two temperatures with each hydrocarbon. Nitrogen atom flow was maintained constant, while butane flow was varied over a wide range.

RESULTS

Hydrogen cyanide was the main product of both the *n*-butane and the isobutane reactions. At 75° C., from 85 to 95% of the *n*-butane consumed was converted to hydrogen cyanide. At 250° C., the yield was from 80 to 90%. At 100° C., from 90 to 97% of the isobutane consumed was converted to hydrogen cyanide, while at 260° C., the yield was from 87 to 95%.

In Fig. 1, hydrogen cyanide production is shown as a function of *n*-butane flow rate. It increased to a maximum at both temperatures, then fell off at higher flow rates. The value of the maximum was higher for the reaction at the higher temperature. Several nitrogen atom – hydrocarbon reactions studied previously (3, 4, 9, 12, 13, 14) have been characterized by complete consumption of nitrogen atoms at high hydrocarbon flow rates. The curves shown in Fig. 1 are, however, incompatible with behavior of this sort.

Hydrogen cyanide production in the isobutane reaction is shown in Fig. 2. As with *n*-butane, the hydrogen cyanide produced from isobutane at 100° C.

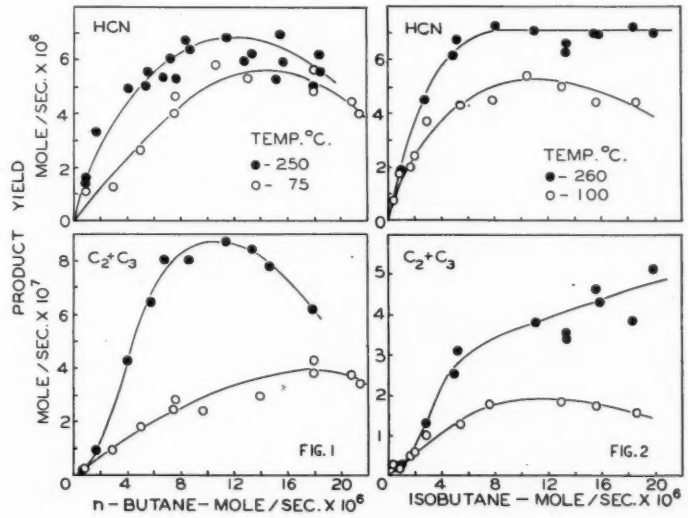

FIG. 1. Rate of formation of products in the nitrogen atom – *n*-butane reaction, as a function of *n*-butane flow rate.

FIG. 2. Rate of formation of products in the nitrogen atom – isobutane reaction, as a function of isobutane flow rate.

We are grateful to Dr. H. I. Schiff of this department for making the mass spectrometer analyses reported in this paper.

passed through a maximum, apparently without complete consumption of nitrogen atoms. At 260° C., however, consumption of nitrogen atoms appeared to be complete, since hydrogen cyanide production increased to a value of about 7.5×10^{-6} mole/sec., and remained constant, within experimental error, with increasing isobutane flow. Further evidence that the value of hydrogen cyanide production represented complete consumption of nitrogen atoms was obtained by making several experiments with ethylene at 250° C. Previous studies (13) have indicated rather clearly that, beyond a fairly well defined flow rate, this reaction occurs with complete consumption of nitrogen atoms. The maximum hydrogen cyanide production was approximately the same as that from the isobutane reaction at 260° C.

Dilution effects and reduction in reaction time at high hydrocarbon flow rates might explain the incomplete consumption of nitrogen atoms at 100° C. in the butane reactions, but cannot account for the maxima in the hydrogen cyanide curves with increase in butane flow rate. However, the reaction flame at these high butane flow rates is located in the narrow neck at the top of the reaction vessel, where surface effects might become important, and surface recombination of nitrogen atoms or destruction of nitrogen–butane reaction complexes could explain the observed decrease in reaction at high butane flow rates.

The hydrocarbon fractions obtained by distillation at −170° C. and −147° C. were found by absorption analysis to be 95 to 100% unsaturated. Mass spectrometer analysis indicated incomplete separation of the unsaturates, with acetylene and ethylene occurring in both fractions. By plotting the sum of these fractions against butane flow, consistent curves were obtained, shown in Figs. 1 and 2 for *n*-butane and isobutane respectively. The shapes of these curves offer additional evidence for the incomplete consumption of nitrogen atoms in the *n*-butane reaction at both temperatures and in the isobutane reaction at 100° C. The unsaturated C_2–C_3 hydrocarbons react rapidly with nitrogen atoms; hence, if nitrogen atoms were completely consumed at high butane flow rates a sharp increase in C_2–C_3 recovered would be expected, as observed, for example, in the recovery of ethylene from the reaction of nitrogen atoms with propylene (12). In the *n*-butane reaction, however, and in the isobutane reaction at 100° C., recovery of C_2–C_3 increased to a maximum, then decreased at high butane flow rates, roughly paralleling the hydrogen chloride curves.

In the isobutane reaction at 260° C., on the other hand, the C_2–C_3 recovered shows a marked increase at high isobutane flow rates, indicating complete consumption of nitrogen atoms in this reaction.

Mass spectrometer analyses of the combined C_2–C_3 fractions are shown in Tables I and II for the *n*-butane and isobutane reaction respectively. It is seen that these fractions consist almost entirely of ethylene and acetylene, with small amounts of ethane, propane, and propylene.

Analyses of noncondensable gases showed that in the temperature range investigated, methane was produced in only small quantities (of the order of 5×10^{-8} mole/sec.) in both the *n*-butane and isobutane reactions.

TABLE I
MASS SPECTROMETER ANALYSIS OF COMBINED C_2–C_3 FRACTION OF *n*-BUTANE REACTION PRODUCTS

Temp., °C.	Butane flow, mole/sec.	Combined C_2–C_3 $\times 10^6$	Percentage C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
75	0.875	0.028	57.6	41.6	1.2	—	—
75	7.57	0.285	35.0	64.5	Trace	—	—
75	10.64	0.244	36.0	63.5	Trace	—	—
75	12.95	0.302	30.7	68.6	0.7	—	—
250	4.04	0.428	20.5	68.0	6.0	3.5	2.0
250	8.59	0.804	16.0	67.5	9.6	4.8	2.0
250	11.42	0.877	15.0	67.0	10.0	6.0	2.0

TABLE II
MASS SPECTROMETER ANALYSIS OF COMBINED C_2–C_3 FRACTION OF ISOBUTANE REACTION PRODUCTS

Temp., °C.	Isobutane flow, mole/sec.	Combined C_2–C_3 $\times 10^6$	Percentage C_2H_2	C_2H_4	C_2H_6	C_3H_6
100	10.5	0.18	46.8	51.8	1.3	—
260	4.90	0.29	31.1	62.2	4.6	2.1
260	15.5	0.44	22.3	67.6	6.8	3.1

DISCUSSION

Since no nitrogen-containing product other than hydrogen cyanide was detectable in either of the systems under investigation, the occurrence of hydrogen abstraction reactions to a significant extent would appear to be excluded.

In the *n*-butane reaction, an initial attack at a primary carbon atom seems most probable:

$$N + C_4H_{10} \rightarrow HCN + H_2 + C_3H_7 \qquad [1]$$

Attack at a secondary carbon atom is less favorable energetically and sterically, but probably occurs to some extent.

$$N + C_4H_{10} \rightarrow HCN + H + C_2H_5 + CH_3 \qquad [2]$$

The propyl radical might be expected to react with another nitrogen atom,

$$N + C_3H_7 \rightarrow HCN + H + C_2H_5 \qquad [3]$$

followed by

$$N + C_2H_5 \rightarrow HCN + CH_3 + H \qquad [4]$$

and

$$N + CH_3 \rightarrow HCN + H_2 \qquad [5]$$

However, this reaction sequence cannot account satisfactorily for a C_2–C_3 fraction composed almost entirely of ethylene and acetylene. Some ethylene might be formed by the disproportionation and hydrogenation of ethyl radicals, but at least an equal quantity of ethane must be expected from these reactions (5). Since ethylene reacts much more rapidly than ethane with nitrogen atoms, more ethane than ethylene would be found in the C_2–C_3 fraction.

The presence of acetylene in the reaction products is even more difficult to explain. While small amounts of acetylene might be accounted for by dehydrogenation of ethylene, the quantities found (Table I) cannot be satisfactorily explained in this way. Furthermore, the ethylene – hydrogen atom reaction forms ethane rather than acetylene as the main product (7).

It would seem necessary to postulate the direct formation of ethylene and acetylene by the reaction of nitrogen atoms with *n*-butane or with *n*-propyl radicals. A number of possible reactions could be suggested, but some of these are energetically unfavorable, while others involve the improbable formation of energetically "hot" radicals by decomposition of a collision complex. The least objectionable reaction leading to the formation of ethylene as a product of nitrogen atom attack would appear to be

$$N + C_3H_7 \rightarrow HCN + H_2 + :CH{-}CH_3 \qquad [6]$$

followed by

$$:CH{-}CH_3 \rightarrow CH_2{=}CH_2$$

For acetylene formation, the reaction

$$N + C_3H_7 \rightarrow CH{\equiv}CH + HCN + 2H_2 \qquad [7]$$

seems most probable.

Reactions of the type [6] and [7], especially the latter, are admittedly incompatible with the Rice–Teller principle of least motion. This principle has been concerned mainly with relatively simple processes, involving energies of the order of 100 kcal. or less, whereas the high energy of formation of the C≡N bond (170–200 kcal.), released within a reaction complex, might permit considerably more intracomplex rearrangement than would otherwise be expected.

Another possibility is the attack by a nitrogen atom at a secondary carbon atom of *n*-butane, with similar direct formation of ethylene or acetylene. This is less favorable, however, both energetically and sterically.

The amounts of ethylene and acetylene recovered represent a relatively small fraction of the *n*-butane consumed. However, if it is assumed that the initial attack of the nitrogen atom is rate controlling, the rate of reaction of nitrogen atoms with these unsaturates is roughly seven times faster than the reaction with *n*-butane. Since nitrogen atoms were never completely consumed in the *n*-butane reaction, ethylene, acetylene, and butane would be expected to compete for nitrogen atoms according to their relative reactivities, independently of the sequence of the reactions. Thus the ethylene and acetylene recovered represents only a fraction of the total amounts of these unsaturates formed during the reaction. Making conservative calculations on this basis, it seems probable that close to 50% of the hydrogen cyanide must have been derived from ethylene or acetylene. Thus the reaction of nitrogen atoms with butane would appear to proceed almost exclusively through reactions of the type [6] and [7] rather than [3]. These would be followed by further reactions with nitrogen atoms, as described in previous papers (13, 14).

In the isobutane reaction, the most probable initial step is the attack by a nitrogen atom at a primary carbon atom:

$$N + CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—CH_3 \rightarrow HCN + H_2 + CH_3—\dot{C}H—CH_3. \qquad [8]$$

An attack at the secondary carbon atom is unlikely, both energetically and sterically. Again, it appears necessary to postulate the direct formation of ethylene and acetylene. If the unpaired electron of the isopropyl radical is considered to be localized on the secondary carbon atom, nitrogen atom attack at this point is highly probable:

$$N + CH_3—\dot{C}H—CH_3 \rightarrow HCN + 2CH_3. \qquad [9]$$

Formation of ethylene or acetylene directly in this reaction would involve rather extensive intracomplex rearrangement, and seems unlikely.

There is some evidence, however, that the isopropyl radical may exhibit partial double bond characteristics (10), resonating between the three structures

$$\bar{C}H_3{=}\overset{+}{C}H—CH_3, \quad CH_3—\dot{C}H—CH_3, \quad CH_3—\overset{+}{C}H{=}\bar{C}H_3$$

so that the free electron is shared by the three carbon atoms, making nitrogen atom attack at the terminal carbon atoms much more probable.

Thus the reaction

$$N + CH_3—\dot{C}H—CH_3 \rightarrow HCN + H_2 + :CH—CH_3 \qquad [10]$$

followed by rearrangement of the ethylidene radical, and

$$N + CH_3—\dot{C}H—CH_3 \rightarrow HCN + 2H_2 + C_2H_2 \qquad [11]$$

would seem to be the most probable sources of ethylene and acetylene.

The smaller amounts of ethylene and acetylene recovered from the isobutane reaction would indicate that part of the reaction proceeds through reaction [9].

The small quantities of ethane, propane, and propylene (Tables I, II) may be adequately explained by hydrogen atom and inter-radical reactions.

Second order rate constants were evaluated for both the *n*-butane and isobutane systems, assuming streamline flow (3). These decreased rather markedly at high butane flow rates beyond the maxima in Figs. 1 and 2 and values for butane flow rates above 12×10^{-6} mole/sec. were therefore not included in the average taken to obtain the following summary of the rate constants:

	Temperature, ° C.	k, liter. mole^{-1}. sec^{-1}.
n-Butane	75	9.8×10^4
	250	5.6×10^5
Isobutane	100	2.4×10^5
	260	8.5×10^5

Activation energies and collision rates, Z, were calculated in the usual way. Collision diameters of 3.0×10^{-8}, 4.8×10^{-8}, and 4.66×10^{-8} cm. were assumed for the nitrogen atom, *n*-butane and isobutane respectively (4, 11).

Probability factors and activation energies for the two reactions were estimated to be as follows:

	E, kcal.	P*
n-Butane	3.6	4.5×10^{-4}
Isobutane	3.1	4.4×10^{-4}

* *Values of P shown are averages of those for the two temperatures.*

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NOTE

THE PHOTOLYSIS OF CYCLOHEXANONE IN PRESENCE OF OXYGEN AND OF CARBON DIOXIDE[1]

By J. R. Dunn[2] and K. O. Kutschke

This work arose from an attempted study of the reaction between oxygen and the radicals produced in the photolysis of cyclohexanone. Benson and Kistiakowsky (1) considered the initial step to involve the formation of the pentamethylene-acyl radical:

$$C_6H_{10}O + h\nu \rightarrow (CH_2)_5{\cdot}CO$$

which could break down as follows:

$$(CH_2)_5CO \rightarrow CH_2(CH_2)_3CH_2 + CO.$$

The initial studies on the photolysis in presence of oxygen were made at room temperature, since cyclohexanone is known to autoxidize at temperatures above 100° C. (3). A small amount of carbon monoxide was produced when cyclohexanone and oxygen were mixed at room temperature in the absence of light.

The cyclohexanone–oxygen mixtures were stirred by a magnetic device and illuminated in a cylindrical cell by the full arc from an S-500 Hanovia lamp. The photolysis products were condensed in liquid nitrogen and the non-condensable products (fraction (*a*)) were taken onto a Cu–CuO furnace heated to 220° C. Any residual oxygen was removed by the copper, and carbon monoxide was oxidized to carbon dioxide and measured as such. Two further fractions (*b*) and (*c*) were taken from the products condensable in liquid nitrogen with the aid of a LeRoy–Ward still. The vapor taken at −155° C. contained ethylene and propane, which had been found by previous workers in the photolysis of cyclohexanone alone. It also contained some 50% of carbon dioxide which had not been found in the absence of oxygen.

During later runs in the absence of oxygen, peaks characteristic of ethane, propyne, and acetylene, as well as unidentifiable high mass peaks, occurred in the mass spectrogram of this fraction. Presumably these products arose from the photolysis of polymers which had collected on the windows of the cell. Between runs the cell was raised to a temperature of about 150° and pumped out for several hours but there was, none the less, a marked drop in the total yield of products as the work proceeded.

Fraction (*c*) was taken at −78° C., and was shown mass spectrographically to contain 1-pentene and cyclopentane in the ratio 2.6: 1, both in those experiments where oxygen was present and in its absence. This ratio differed both from that found by Benson and Kistiakowsky (1) and that given by Miller (2). The exact value of this ratio seems to depend upon experimental conditions.

[1]*Issued as N.R.C. 3302.*
[2]*National Research Laboratories Postdoctorate Fellow 1953–.*

The analysis figures for typical photolyses in presence and absence of oxygen are given in Table I.

In presence of oxygen the yield of carbon monoxide is considerably greater than in its absence, while there is a 25% decrease in the yield of C_5's. In the absence of oxygen the yield of carbon monoxide is only slightly greater than

TABLE I
PHOTOLYSIS OF CYCLOHEXANONE (4.5 MM. CYCLOHEXANONE; 27° C.; FOUR HOURS' ILLUMINATION)

Run	CO, cc.	Fraction (*b*), cc.	Fraction (*c*), cc.
A_4 (10 mm. O_2)	1.36	0.29	0.50
A_6 (O_2 absent)	0.77	0.085	0.67

that of the other volatile products. However, when oxygen is present the material balance is poor, indicating that there is some reaction giving rise to much material of high boiling point.

The considerable yield of C_5 fraction in presence of oxygen indicates that oxygen does not react readily either with the pentamethylene-acyl radical or the pentamethylene radical. It is possible that these radicals are formed by a slow step from excited cyclohexanone and that they give rise to 1-pentene and cyclopentane by a very rapid reaction. In such a case the oxygen may act as a quencher of the excited ketone, and this action alone could account for the 25% decrease in C_5 yield.

No previous studies could be found on the course of cyclohexanone photolysis in presence of foreign gases and, in order to test the quenching theory, a number of experiments were carried out in presence of carbon dioxide at various pressures. In Table II the yield of carbon monoxide, which, in absence of oxygen is 10–15% higher than that of C_5's, is given together with the pressures of carbon dioxide.

TABLE II
PHOTOLYSIS OF CYCLOHEXANONE IN PRESENCE OF CARBON DIOXIDE (FOUR HOURS' ILLUMINATION)

Run	Pressure, mm. Cyclohexanone	Pressure, mm. CO_2	CO, cc.
	Runs at 27° C.		
A_9	5.0	0	0.13
A_{12}	5.0	0	0.137
A_{16}	5.3	0	0.096
A_{11}	5.2	10	0.090
A_{15}	4.5	20	0.073
A_{14}	4.5	30	0.058
A_{13}	5.0	50	0.053
	Runs at ~ 150° C.		
A_{18}	4.5	0	0.100
A_{19}	4.8	50	0.091

The accuracy of these figures is, undoubtedly, low owing to the decrease in light intensity as the products from subsequent runs deposited on the cell. The fact that the polymeric deposit was slightly charred by heat treatment in an attempt to dislodge it will probably account for the lowered yields in A_9,A_{12}, and A_{16}, Table II (cf. A_6, Table I). However, the trend toward low efficiencies at high carbon dioxide pressures is marked, and quenching of excited cyclohexanone by carbon dioxide would be consistent with this.

At higher temperatures ($\sim$150° C.) the quantum yield in the uninhibited reaction is almost unchanged (1, 2) but the quenching effect is far less marked.

Owing to the interference of polymeric products, and also of autoxidation at higher temperatures, it is impracticable to investigate the reaction between oxygen and the radicals from cyclohexanone photolysis more fully. However, the quenching effect of foreign gases on the photochemical decomposition of cyclohexanone is interesting and unusual, and similar studies on cyclopentanone might be profitable.

We wish to thank Dr. E. W. R. Steacie for his constant interest in this work, and we are indebted to Miss Frances Gauthier and Miss June Fuller of these laboratories for mass spectrographic analyses.

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